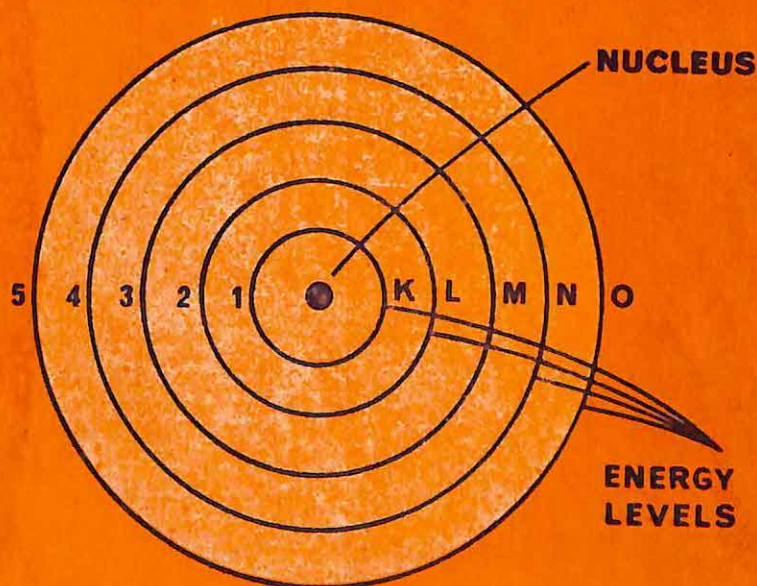


FUNDAMENTALS OF CHEMISTRY

VOL. I

D.P. GOEL - S.P. MITTAL



PITAMBAR PUBLISHING COMPANY

FUNDAMENTALS OF CHEMISTRY

VOL. I



Strictly according to the latest syllabus prescribed by the Central Board of Secondary Education, New Delhi, in Chemistry for Class IX of Secondary School Examination, 1987 and onwards for the Delhi & All India Schemes.

FUNDAMENTALS OF CHEMISTRY

VOL. I
(FOR CLASS IX)

BY

D. P. GOEL

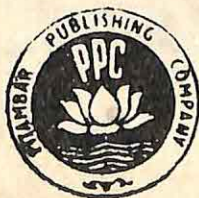
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PREFACE

This book is intended for class IX students. It gathers together the requirements of the latest syllabus developed jointly by National Council of Educational Research and Training (NCERT) and Central Board of Secondary Education (CBSE). Also, it takes into consideration not only the topics but the objectives set by the syllabus as well. The NCERT has already brought out its own text covering the syllabus. Why then the present book? It is an attempt to offer a simpler yet exhaustive exposition of the subject; it is an assurance to equip the students with all informations and methods for an excellent performance in their examination. This book also meets the requirements of the students appearing for secondary examination of Delhi Board of Secondary Education.

In planning this book, we have adopted the following general principles :

- Each unit is prefaced with a list of *learning objectives*. The purpose of these objectives is to apprise the students of the scope of the unit.
- *Experiments* have been included to complement a course of practical work. Experiments will make the learning process easier for students.
- Answers to the questions given in the NCERT text have also been included.
- At the end of each unit, *Unit Through Exercises*, has been included. It is an integral part of the text. Here the subject-matter is presented in a question-answer format with the dual purpose of providing the subject-matter to the students in a crisp form, and for aiding them in preparing for the examination.
- At intervals in units 5 and 6, *work exercises* are included so that students can pause and test their understanding.
- Numerous *illustrations and diagrams* have been embodied in the text. These present most of the topics in visual terms.
- At the end of each unit a collection of *review questions* has been provided, which cover the whole unit and whose aim is not merely to test the reader's knowledge, but also to promote understanding and to stimulate further thought.
- Explanation of *important terms and concepts* of the subject at the end of each unit reinforces the text.
- *Presentation* of the subject matter has been done in a sound, lucid and simple manner to help the students of all levels.

Care has been taken over the layout of each page so as to present the subject vividly, fitting figures, graphs and tables to reinforce the text. The review questions at the end of each unit vary in style and these may be used in tests, in class room discussions in class and/or home work.

We hope the teachers will encourage the students to cover parts of the syllabus on their own from the text book in hand, duly assisted by the various items included in the present work such as learning objectives, work exercises, planned experiments, unit through exercises and objective questions. These items are designed to reduce the amount of note-making. The time thus saved may be more profitably used for discussions and laboratory work.

We would whole-heartedly welcome comments and suggestions from students and teachers.

This volume has been widely acclaimed by everyone. We have received letters of appreciation from both students and teachers.

D.P. GOEL
S.P. MITTAL

SYLLABUS PRESCRIBED BY CBSE, NEW DELHI

Class IX

Time : 1½ Hrs

Marks : 50

		Weightage (Marks)
Unit I	Nature and Composition of Matter	8
Unit II	Substances—their Separation and Purification	3
Unit III	Structure of Atom and Chemical Bonding	7
Unit IV	Periodic Classification of Elements	5
Unit V	Chemical Reactions : How Fast and How Far	7
Unit VI	The Non-Metals	10
Unit VII	Some Useful Compounds	5
Unit VIII	Pollution and its Effects on the Living World.	5

General Objectives :

1. To enable the students to recognize the role of Chemistry in day-to-day life.
2. To develop an understanding of the basic concepts in Chemistry which would provide a background for learning Chemistry at Senior Secondary level.
3. To promote interest in students for Chemistry and enable them to use Chemistry as an important subject for industries.
4. To develop in students a familiarity with Chemistry as General Science and with its inter-disciplinary aspects.
5. To develop experimental skills in students necessary for the analysis of simple compounds used in their daily life.
6. To develop scientific attitude and give training in scientific methods.
7. To arouse in the young mind a spirit of scientific enquiry about the nature of material substances and the changes they undergo.
8. The course provides a base for students who wish to take Chemistry at plus two stage and it will also benefit those who are not going to continue the subject further.

1. NATURE AND COMPOSITION OF MATTER

Periods : 10

The main purpose of this unit is introductory. As such, it provides information about the various types of aggregates of matter (elements, compounds and mixtures, or solids, liquids and gases). This understanding about the nature of matter is built up on ideas of atomic and molecular composition. The skills of understanding and using the language of Chemistry are also built up in this unit. Being the first unit, it is also to some extent recapitulative and serves as a link between what the students have learnt at middle level and what they would learn in secondary classes.

Contents

Classification of matter, Elements, Compounds, Mixture, Atomic and Molecular Masses, Formula of a compound—how to write it and what does it convey. Chemical Equation—Meaning, how to balance them (trial and success method only) Avogadro's Laws.

Mole, gram atomic-mass, gram molecular mass, Relationship between mass and number of molecules, volumes and number of molecules of gas at STP. States of matter, molecular arrangement in the three states of matter, Effect of pressure and temperature on the volume of a gas. Gas Equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Simple numericals on mole concept, gas laws and gas equation involving one stage.

Suggested Approach

Teachers may demonstrate the advantages of classification of elements taking examples from the everyday life of students. They may encourage students to prepare a cardboard box (vol. 22.4 litres) to enable them to grasp this idea of the size of the gram molecular volume. Teachers may demonstrate variations in gas volume using air thermometer, hot water and ice. They may emphasize that balancing and completion of equation does not mean that such a chemical reaction can occur.

Students may be given clear understanding as to why the equation $2\text{KNO}_3 \rightarrow 2\text{KNO}_2 + \text{O}_2$ is not written as $\text{KNO}_3 \rightarrow \text{KNO}_2 + \text{O}$.

2. SUBSTANCES—THEIR SEPARATION AND PURIFICATION

Periods : 5

Many of the substances used daily are either mixtures or form mixtures during their preparation. This unit is by and large an experimental one. While in Unit 1 the stress was on development of a conceptual basis of understanding and interpretation of chemical phenomenon, here in this unit the emphasis is on development of basic experimental skills relevant for work in Chemistry. As far as possible, the apparatus and materials used are common and of everyday use so that students of all schools may be exposed to this simple type of experimental work. If a new concept (e.g. colloidal solution) has been introduced in this unit (and this is quite rare), the approach/treatment is operational (or practical).

Stress should, therefore, be on learning of skills through actual experimentation by students (in groups or individually) rather than on teaching its contents through lectures or even lecture-cum-demonstrations.

Contents

Mixture and compounds—how to distinguish them, solutions and suspensions, how to identify them, Methods of separation of components of a mixture, pure substances how to identify them.

Suggested Approach

The following mixtures may be got separated either in groups or demonstrations may be arranged to show the separation of mixtures.

Mixture of Sugar and Sulphur, mixture of charcoal powder and Sulphur powder, mixture of sand, Sulphur and Sodium chloride, Mixture of Sodium chloride, Sand and Ammonium chloride, Mixture of oil and water, Mixture of Alcohol and water.

3. STRUCTURES OF ATOM AND CHEMICAL BONDING

Periods : 7

'Structure' is a fundamental concept in the development of any framework of (conceptual) understanding. The behaviour of any sample of matter towards another would depend on their respective properties, and the properties are dependent on inherent structure of the interacting samples of matter. The concept of structure, in terms of atoms and molecules composing matter, was introduced in Unit 1. Herein, it is further elaborated and specified in

the sense that the structure of building-blocks of all chemical substances (*i.e.* atoms) has been taken up for study.

The notion of structure involves the concepts of (a) 'elements of structure' (*i.e.* proton, neutron, electron in the case of atom) and the (b) organisation or arrangement of elements of structure (*e.g.* electronic configuration). With this basis of understanding in respect of structure at atomic level the idea of the structure of molecules has been developed in terms of different types of chemical bonding.

Contents

Simple idea about mass and charge of electrons, protons and neutrons. Rutherford's experiment conclusions, Bohr's concept of an atom, Atomic number and Mass number.

Distribution of electrons in various energy levels of first 20 elements, Isotopes—definition and importance, chemical bond—meaning and how it is formed, electrovalent and covalent bonds—how they are formed, properties of electrovalent and covalent compounds.

Suggested Approach

Teachers may encourage their students to build up the ground state models of the atoms of the elements. They can also demonstrate the formation of molecules with the help of wooden spheres and sticks or rubber balls and glue. Electrical conductivity in ionic and covalent compounds may also be demonstrated. Special attention needs to be given to the development of accurate observational skills in students so that they are able to record correctly the melting points of : urea, common salt, sugar, potassium-iodide, and boiling point of carbon, tetra chloride, alcohol, benzene etc. from the book of constants.

4. PERIODIC CLASSIFICATIONS OF ELEMENTS

Periods : 4

In the earlier unit there was an attempt to bring an order into the variety of atoms of different elements by considering them as built up of a few fundamental units, namely, protons, neutrons and electrons. The structure of atoms was shown to vary from one element to the next in a very systematic way (increase of one positive charge in the nucleus, and consequently one more electron outside the nucleus). The discussion was, by and large, on the micro-level of either individual atoms, or molecules formed by interaction of atoms.

In our everyday world we, however, come across and deal with a variety of substances, their properties and their behaviour towards one another at a macro-level. 'Classification' has been the age-old method for dealing with this variety of materials and phenomena. The problem of classification of elements has been discussed and presented a bit historically to show an evolutionary trend on the basis of classification used at different times. Classification based on nuclear charge (*i.e.* atomic number) of the atom has been shown to be the latest and most satisfactory. The gulf between the micro-world of atoms/molecules and the macro-world of elements/compounds is thus bridged by basing classification at macro-level on the corresponding structures at micro-level (*i.e.* electronic configuration).

Contents

Classification, need for classification of elements, early attempts for classification of elements—Dobereiner, Newlands, Lothar Meyer. Mendeleev's Modern periodic table—groups, periods, transition elements. Gradation of properties in groups and periods—electro-negative and electropositive character, atomic size, density, boiling, and melting points.

Suggested Approach

To give training in classification students may be provided with names of several elements, their physical and chemical properties and they be asked to classify them into metals and non-metals. Students may draw diagrams of atomic structure of a number of elements and asked to arrange these diagrams to show the periodic recurrence of properties. The teachers may build a periodic table using modelling clay balls made to the relative size of the atoms. (Use a scale $1\text{ \AA} = 1\text{ cm}$).

5. CHEMICAL REACTIONS—HOW FAST AND HOW FAR

Periods : 7

Ours is a world of not only chemical substances (in all their vast variety of elements, mixtures and compounds) but also chemical and physical phenomena. Just as there is a great variety in substances around us in terms of properties and structure (systematised in units III and IV), there is a variety in their capacity to react with one another. Chemical reactions may be of an endless variety. There is an elementary attempt in this unit to bring order into our knowledge of chemical reactions. The knowledge gained earlier has been used and elaborated further to develop an understanding of the world of chemical phenomena.

Contents

Meaning of chemical reaction, types of chemical reactions, Redox reactions in terms of exchange of electrons, Exothermic and Endothermic Reactions, Electrolysis and its applications, Rate of chemical reaction—its meaning, factors affecting rates of a reaction, Reversible Reactions and Chemical Equilibrium, Physical Equilibrium, Ionic Equilibrium. Ionization of water, significance of pH scale. Importance of pH in agriculture and human body. Factors affecting Chemical Equilibrium.

Suggested Approach

Teachers may explain the effect of concentration on rate of reaction with the help of experiments : Magnesium ribbon and hydrochloric acid of different concentrations may be tried. The effect of temperature on rate of reaction may be studied with hydrochloric acid at different temperatures (when it reacts with a given amount of Zinc (about 0.5 g) and noting the time for disappearance of Zinc. In order to explain the dynamic character of equilibrium an irregularly shaped crystal of Sodium chloride (retaining constant size) in the saturated solution of the salt can be shown to students.

6. THE NON-METALS

Periods : 10

This unit deals with a broad category of elements namely, the non-metals. A few representative elements have been taken up for study in some details. The traditional aspects of a systematic study of Chemistry (preparation, properties, uses etc.) have been covered. The experimental and application aspects have been stressed. It is hoped that a few gases will be prepared and studied by the students to give them a taste of chemistry in the laboratory.

Contents

General characteristics of Non-Metals

Hydrogen, Oxygen and Sulphur—their occurrence and uses.

Hydrogen Sulphide and Sulphur Dioxide—their occurrence, laboratory preparation, properties, and uses.

Sulphuric Acid—Major sulphuric acid plants in India, Manufacture by contact process (principle only) properties, uses and test for sulphuric acid.

Nitrogen—its occurrence and uses.

Ammonia—its occurrence, laboratory preparation, properties, uses and test.

Nitric Acid—its occurrence, manufacture (principle only), properties, uses and test.

Phosphorus—its occurrence and uses.

Halogens—their occurrence in nature, laboratory preparation, properties, uses and tests of chlorine, and *hydrogen chloride*. Preparation of *hydrochloric acid* and *fresh hydrogen chloride*. Distinction between chloride, bromide and iodide. Distinction between *hydrochloric acid*, *Nitric acid* and *Sulphuric acid*.

Suggested Approach

Teachers may make use of models to explain the formation of O_2 and S_8 molecules. If time permits, students can prepare allotropic forms of sulphur and observe them through the magnifying glass. Teachers may demonstrate the properties of nitric acid with the active participation of students which may include activities such as (i) display of compounds containing nitrogen and phosphorus. (ii) observing the piece of greased cloth after dipping it into the solution of NH_3 in water, and (iii) Collecting the names of commonly used smelling salts.

7. SOME USEFUL COMPOUNDS

Periods : 4

Some elements form basic oxides while others form acidic oxides. Interaction of acidic and basic oxides results in the formation of salts. The underlying theme of this unit is to give students an idea that Chemistry—Its principles, understanding, its knowledge about facts and phenomena are integral part of our life.

Contents

Calcium oxide, calcium hydroxide, sodium carbonate, copper sulphate, Bleaching powder, plaster of Paris, Sodium Nitrate their preparation (Principle only), and uses specifying the properties involved.

Suggested Approach

Teachers may ask students to display compounds like calcium oxide, calcium hydroxide, sodium carbonate, calcium sulphate, bleaching powder, plaster of Paris and sodium nitrate in transparent containers and list out the uses of these compounds in everyday life. Wherever possible, teachers may arrange class visit to water treatment plant or the lime kiln, subsequently prepare a report based on their experiences.

8. POLLUTION AND ITS EFFECTS ON THE LIVING WORLD

Periods : 3

Intensive application of Chemistry while providing comforts to all of us has created number of problems that affect the quality of life. Pollution of air, water and soil is one of the common concern of the modern world. This unit sensitizes the students about the hazards of pollution so that they become aware of the need for clean environment for the survival of human race.

Contents

Pollution—its meaning and effect on gravity of life, air pollution, water pollution, soil pollution—their causes and methods to check them.

Suggested Approach :

Teachers may ask the students to prepare a chart listing the common air pollutants of the locality. A visit can also be arranged to an area which is overwhelmingly misty where students test the acidity of mist with the help of litmus paper or pH paper. Activities like debates on the use of fertilizers, insecticides and pesticides on soil fertility can also be organized in school.

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8. POLLUTION AND ITS EFFECTS ON THE LIVING WORLD

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UNIT 1

Nature and Composition of Matter



John Dalton
(1766-1844)

John Dalton advanced the atomic theory. According to him atoms are the building blocks of all matter. He was the first to state the law of multiple proportions.

Learning Objectives

At the completion of this unit, you should be able to :

1. Define matter.
2. Classify and give examples of types of matter.
3. List the states of matter.
4. Define element, compound and mixture.
5. Explain the atomic theory with a mental picture.
6. Write the correct symbols for many elements.
7. Define the law of definite composition.
8. Define the law of conservation of matter.
9. Write formulae from the given names of compounds.
10. Balance chemical equations by different methods.
11. Define atomic mass, molecular mass and atomic mass unit.
12. Define the term mole.
13. Calculate the molar masses of elements and compounds.
14. Find the number of moles of a substance when the mass is given.
15. Explain the significance of Avogadro's number.
16. Explain the significance of STP.
17. Define various gas laws with illustrations.
18. Derive a relationship between pressure, volume and temperature.

1-1 INTRODUCTION

Many questions occur to students as they begin any new course of study. What is it? What is chemistry?? How can I study it most efficiently? In this spirit, we will write briefly about chemistry.

Chemistry is a science that deals with the structure and behaviour of the materials. Materials are samples of matter; they include metals, plants, animals, rocks, gases, paints, plastics, explosives, etc. Regardless of whether the matter is natural or synthetic, it is composed of ultimate particles called atoms and molecules. Chemists are interested in the varieties of matter and what changes they undergo.

Matter is any material thing that occupies space (or volume) and has mass. For example, water, a cube of sugar or a shirt has mass and volume. The volume and mass of an object are related by a property called density. Density is defined as weight over volume,

$$\text{density} = \frac{\text{weight}}{\text{volume}}$$

$$\text{weight} = \text{density} \times \text{volume}$$

There is a difference between the mass of an object and the weight of an object. The mass is an inherent property, while the weight

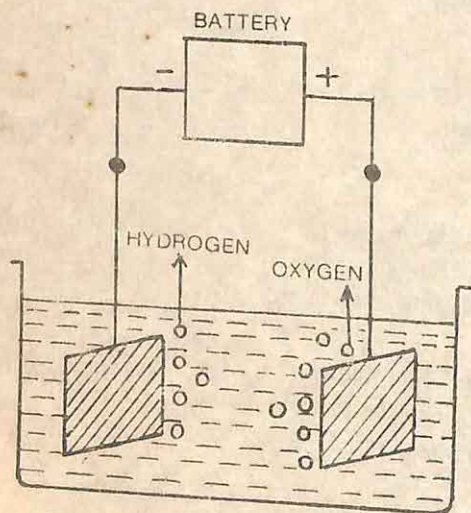


Fig. 1-1. Electrolysis of water forming hydrogen and oxygen (elements)

is a result of the mass and the gravitational attraction. The terms 'mass' and 'weight' are often used interchangeably since the earth's gravitational attraction is essentially constant.

1-2 CLASSES OF MATTER

Mixtures. A substance is recognized by its physical and chemical properties. Chemists always use physical and chemical properties to describe and identify a substance. Substances can be classified on the basis of their chemical nature. Most of the materials such as air, milk, gasoline and steel are mixtures. Mixtures contain two or more distinct substances that can be physically separated from each other. Mixtures are broadly divided into two categories: heterogeneous and homogeneous. Heterogeneous mixtures are not uniform throughout rather different components of the mixture occupy distinct regions within the sample. A mixture of iron and sulphur is a heterogeneous mixture. The constituents of this mixture can be separated by simple methods. Homogeneous mixture has the same composition throughout the entire sample. Air, milk, water and alcohol are examples of homogeneous mixtures.

Elements and Compounds Water can be decomposed into hydrogen and oxygen by passing an electric current through water (Fig. 1-1). In this decomposition reaction water is broken into two simpler substances. But

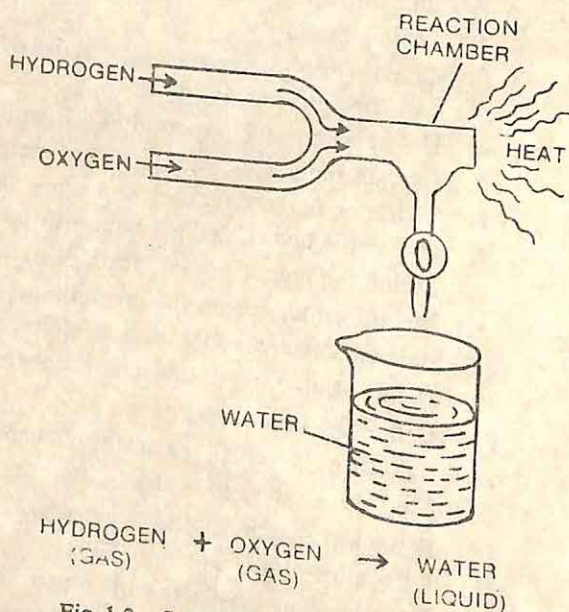


Fig. 1-2. Synthesis of water (compound) from hydrogen and oxygen

these substances hydrogen and oxygen can never be broken apart into simpler substances. These substances which cannot be broken down into other substances are called elements. Lead, iron, mercury and sulphur are examples of elements. Pure substances that can be decomposed or synthesized are compounds of their constituent elements. Water is a compound of hydrogen and oxygen; table salt is a compound of sodium and chlorine; and sugar is a compound of carbon, hydrogen and oxygen. In Fig. 1-2, water is synthesized from its constituent elements hydrogen and oxygen.

So far 106 elements are known. Nine elements were known before the time of Christ—copper, gold, iron, mercury, silver, tin, lead, sulphur and carbon. Over 90 percent of the human body is composed mainly of three elements, *i.e.*, oxygen, carbon and hydrogen. Every element has been assigned a symbol, for example, (Cu) for copper, (Fe) for iron, (Na) for sodium, (Au) for gold and (Ag) for silver.

Table 1-1 summarizes the differences between elements, compounds and mixtures.

Experiment 1-1. To separate components of mixtures of two substances one of which is magnetic in nature. Bring a magnet near iron filings (Fig. 1-3). The magnet attracts iron. Now cover iron filings with sulphur. Since the two elements on mixing together do not undergo any chemical change,

they will continue to retain their characteristics. The magnet dipping into the mixture is able to attract iron particles. Before any reaction between iron and sulphur, iron is attracted by magnet. But when it combines with sulphur it forms a new substance. The new substance is not attracted by magnet because it has properties different from iron.

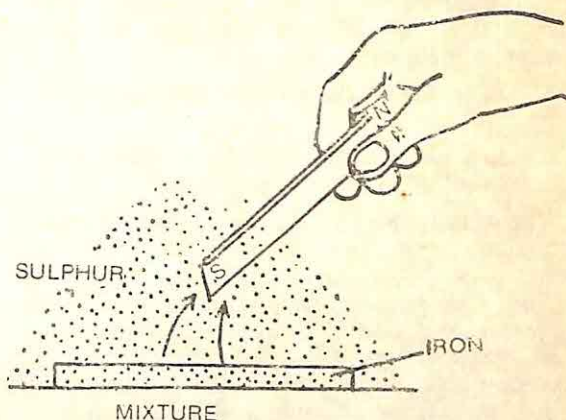


Fig. 1-3. Separation of a mixture—iron and sulphur

1-3 THE ATOMIC THEORY

To explain various observations and to understand chemical reactions, John Dalton in the early 1800's proposed a theory. This

Table 1-1 Differences between elements, compounds and mixtures

<i>Elements</i>	<i>Compounds</i>	<i>Mixtures</i>
1. Cannot be broken down into anything simpler.	1. Can be broken down into constituent elements.	1. Substances in a mixture can be present in any proportion.
2. Combine to form compounds.	2. Have properties different from the constituent elements.	2. Substances in a mixture retain their individual properties.
3. Composed of only one type of atoms.	3. Elements are present in a definite and fixed proportion by mass.	

is the atomic theory, which contains the following hypothesis :

1. Matter (or element) is composed of tiny fundamental particles called atoms (from the Greek 'atomos' meaning indivisible).
2. Atoms of an element are similar (same mass and size) but differ from atoms of other elements.
3. Atoms enter into combinations with other atoms of different elements or same element to form compounds.
4. Atoms are indestructible and cannot be created.
5. In a given compound the relative number and kind of atoms are constant.

The atomic theory was and is very important, since it provides a mental picture of matter (Fig. 1-4). An atom can be pictured as a tiny spherical particle. An atom is the smallest representative particle of an element. Each element has a unique kind of atom, and each atom has mass. The masses of atoms of various elements differ from one another. Compounds involve atoms combined in definite ratio. In mixtures, the atoms of different elements are present in an uncombined state without any definite ratio.

Dalton's atomic theory explains several simple laws known at the time of its inception. The *law of conservation of mass* is a logical consequence of Dalton's atomic theory. As atoms can neither be created nor destroyed in a chemical reaction, and since all matter consists of atoms, a chemical reaction neither creates nor destroys mass.

Dalton's theory also explained the *law of definite proportions* or *law of constant composition*. Compounds involve definite combination of atoms, i.e., a given compound will always include the same atoms in the same relative amounts. For example, water always contains two atoms of hydrogen combined with every atom of oxygen (Fig. 1-5).

John Dalton refused to accept the existence of elements composed of diatomic molecules, though there was solid experimental evidence of the existence of diatomic molecules. Table 1-2 presents the elements that are made up of diatomic molecules.

Table 1-2 Diatomic molecules of the elements

Element	Molecule of the element
Hydrogen	H ₂
Oxygen	O ₂
Nitrogen	N ₂
Chlorine	Cl ₂
Bromine	Br ₂

A molecule can be defined as a collection of two or more atoms held together strongly enough to form an individual particle. Molecules formed from the same kind of atoms is a molecule of an element (Table 1-2). Molecule formed from the combination of different kinds of atoms is a molecule of a compound. For example, a molecule of compound, say hydrogen chloride, is formed by the combination of one atom of hydrogen and one atom of chlorine.

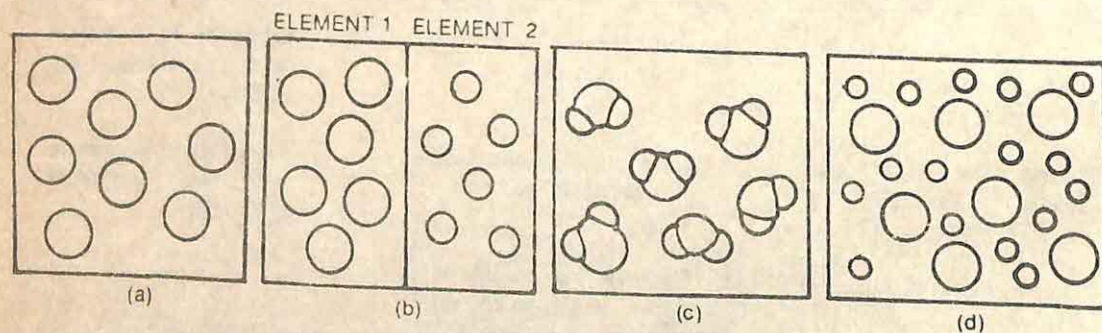
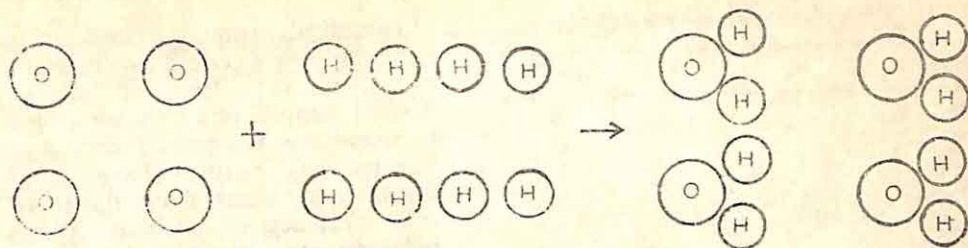
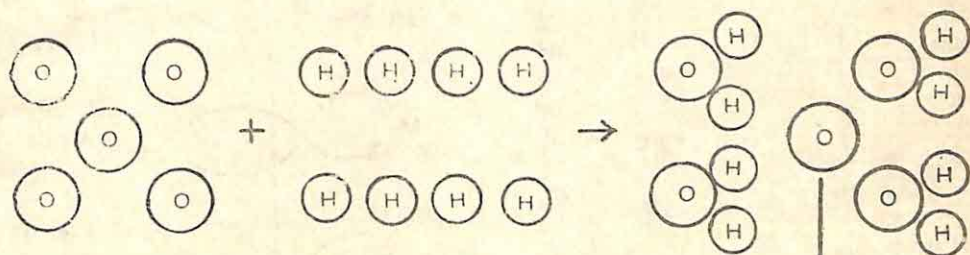


Fig. 1-4. Illustration of the atomic theory

- (a) The atoms of a given element are alike
- (b) Different elements have different atoms
- (c) Compound of elements
- (d) A mixture composed of atoms of elements

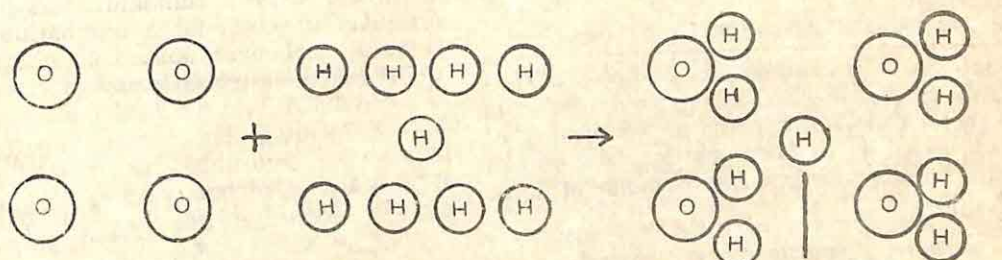


(a) HYDROGEN AND OXYGEN ATOM IN PROPER RATIO



(b) AN EXCESS OF OXYGEN MIXED WITH HYDROGEN

ONE OXYGEN ATOM REMAINS UNCHANGED



(c) AN EXCESS OF HYDROGEN MIXED WITH OXYGEN

ONE HYDROGEN ATOM REMAINS UNCHANGED

Fig. 1-5. Law of definite proportions.

1-4 SYMBOLS, FORMULAE AND EQUATIONS

John Dalton assigned pictorial symbols to oxygen, hydrogen, carbon and nitrogen as follows:

OXYGEN



HYDROGEN



CARBON



NITROGEN



Today, chemists use a symbolic system which is different from the one proposed by Dalton. Each element has a name which in many cases was given to it by its discoverer. The *symbol* consists of one or two letters taken frequently, but not always, from the first two letters in the name of the element. Some symbols are derived from the Latin name of the element. Symbols of some common elements are provided in Table 1-3.

The symbols find their most important use in writing a compound by a *formula*. The formula indicates both nature and relative number of atoms of each element in a compound.

Table 1-3 Elements and their symbols

Element	Symbol
Boron	B
Carbon	C
Fluorine	F
Hydrogen	H
Iodine	I
Nitrogen	N
Oxygen	O
Phosphorus	P
Sulphur	S
Aluminium	Al
Barium	Ba
Calcium	Ca
Bromine	Br
Helium	He
Nickel	Ni
Silicon	Si
Antimony (Stibium)	Sb
Copper (Cuprum)	Cu
Gold (Aurum)	Au
Iron (Ferrum)	Fe
Lead (Plumbum)	Pb
Mercury (Hydrargyrum)	Hg
Potassium (Kalium)	K
Silver (Argentum)	Ag
Sodium (Natrium)	Na
Tin (Stannum)	Sn

Note : Names in parantheses are Latin names.

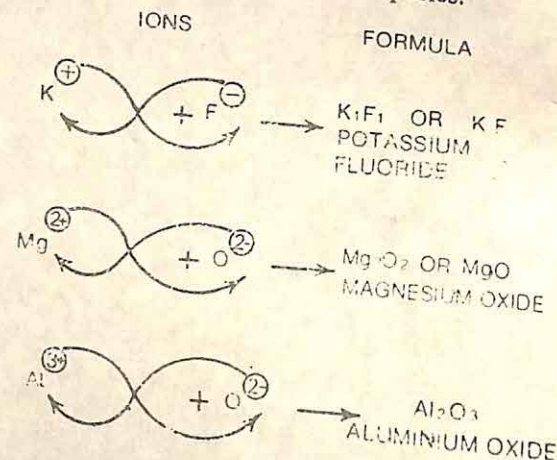
compounds. For example, the compound H_2O consists of 2 atoms of hydrogen and one atom of oxygen ; $C_6H_{12}O_6$ consists of six atoms of carbon, 12 atoms of hydrogen and 6 atoms of oxygen. Table 1-4 lists the formulae of some compounds.

Table 1-4 Formulae of some compounds

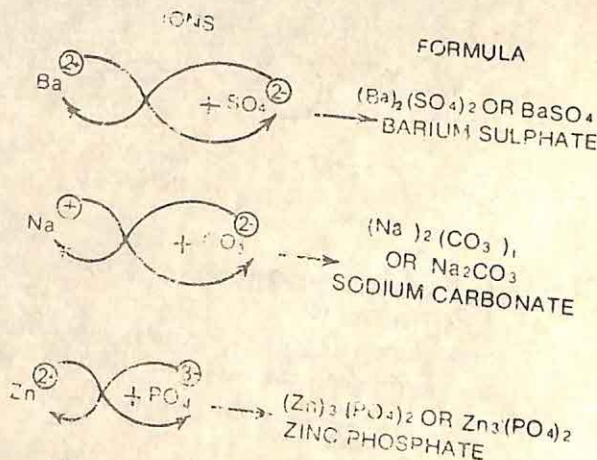
Water	H_2O
Carbon monoxide	CO
Carbon dioxide	CO_2
Sodium hydroxide	$NaOH$
Sulphuric acid	H_2SO_4
Carbon tetrachloride	CCl_4
Benzene	C_6H_6
Methane	CH_4
Ammonia	NH_3

Some compounds are composed, not of molecules, but of ions. Ions are atoms or a group of atoms that carry electrical charges. The formula of a compound does not indicate how the atoms combine but it gives the number

of combined atoms. Atoms of the elements combine with a certain capacity which is known as *valence* or *valency* of the elements. In writing formula of a compound, it is important to know the valence of combining elements. Species with positive charge is placed first in formulae but apart from this there is no fixed rule. Valency of positive species is written below negative species and valency of negative species is written below positive species.



There are many radicals (or ions) containing more than one element, e.g., nitrate NO_3^- , carbonate CO_3^{2-} , sulphate SO_4^{2-} , etc. The formulae of compounds like barium sulphate, sodium carbonate and zinc phosphate are written in the same fashion.



The Table 1-5 indicates valencies of ions in some common compounds.

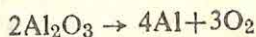
A **chemical equation** represents an actual chemical reaction with the help of symbols

Table 1-5 Valencies of ions in some common compounds

Compound	Formula	Constituent ions	Valencies
Aluminium oxide	Al_2O_3	Al^{3+} O^{2-}	3 2
Calcium carbonate	CaCO_3	Ca^{2+} CO_3^{2-}	2 2
Sodium nitrate	NaNO_3	Na^{+} NO_3^{-}	1 1
Barium chloride	BaCl_2	Ba^{2+} Cl^{-}	2 1
Potassium hydroxide	KOH	K^{+} OH^{-}	1 1
Copper phosphate	$\text{Cu}_3(\text{PO}_4)_2$	Cu^{2+} PO_4^{3-}	2 3
Zinc nitrate	$\text{Zn}(\text{NO}_3)_2$	Zn^{2+} NO_3^{-}	2 1
Mercury (I) chloride	Hg_2Cl_2	Hg_2^{+} Cl^{-}	1 1
Mercury (II) chloride	HgCl_2	Hg^{2+} Cl^{-}	2 1
Iron (II) oxide	FeO	Fe^{2+} O^{2-}	2 2
Iron (III) oxide	Fe_2O_3	Fe^{3+} O^{2-}	3 2

Note : The Roman number in parantheses shows the valency state of the element.

and formulae of products and reactants. For example, aluminium metal is obtained by decomposing aluminium oxide into its elements. On writing the symbols and formulae of all the substances, we get the following chemical equation :



Equations tell us not only what substances react together or are involved but also what amounts of substances are involved. Numbers such as 2, 3, 5 or 9 etc. written before symbols or formulae signify that equation satisfies the law of conservation of mass. When an equation indicates that the law of conservation of mass is satisfied, the equation is said to be balanced.

A chemical equation is written as follows :

(i) Write the correct symbols and formulae of the reactants on the left and separate them by plus (+) sign.

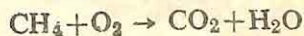
(ii) Write the correct symbols and formulae of the products on the right and separate them by (+) sign.

(iii) An arrow ($\rightarrow$) is written between the reactants and the products to indicate the direction in which the reaction takes place. This gives us a skeleton equation. To get a balanced equation, the number of atoms of various elements on both sides are equalised.

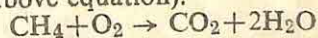
There are two methods of balancing a chemical equation : (a) the hit and trial method, and (b) the partial equation method.

(a) **The hit and trial method :** The various steps of this method are :

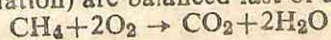
(i) Write the skeleton equation, e.g.,



(ii) Equalise the atoms of the elements which occur at the minimum number of places (H in the above equation).



(iii) The atoms of the elements which occur at the maximum number of places (O in the above equation) are balanced last of all.



This method can be conveniently used for simple equations only.

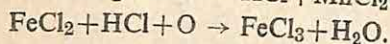
(b) **The partial equation method:** Equations which are difficult to balance by hit and trial method are balanced by the partial equation method. For example, the equation



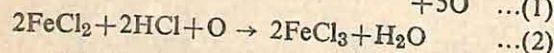
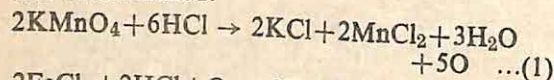
is difficult to balance by hit and trial method. It is balanced by the partial equation method as follows:

(i) The reaction is supposed to take place in two or more steps

(ii) Write partial equations for the various steps.

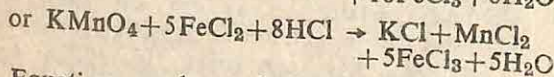
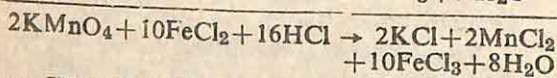
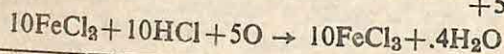
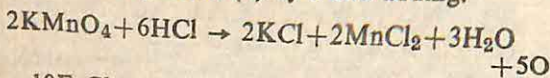


(iii) Balance the partial equations by hit and trial method.



(iv) Multiply the partial equations throughout with a suitable coefficient to cancel out intermediate products which do not appear in the final equation. Add the partial equations to get the final balanced equation.

The product (O) which does not appear in the final equation, is cancelled out by multiplying partial equation (2) by 5 and adding.



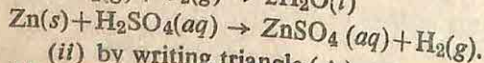
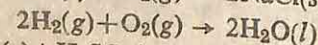
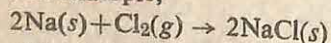
Equations can be made more informative:

(i) by using the following notations for the physical states of reactants and products:

(s) = solid, (g) = gas or vapour

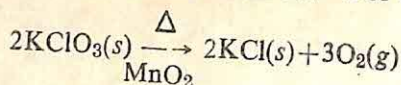
(l) = liquid, (aq) = aqueous (water solution)

For example,

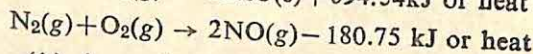
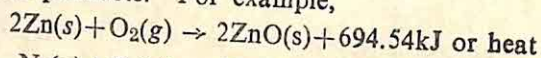


(ii) by writing triangle (Δ) over an arrow. The sign indicates that heating causes the reaction to proceed.

The catalyst used in the reaction is written below the arrow. For example,



(iii) by indicating the heat changes taking place in the reactions. Reactions in which heat is evolved are called exothermic reactions, and reactions in which heat is absorbed are called endothermic reactions. Exothermic and endothermic reactions are represented by writing +heat and -heat, respectively, with the products. For example,



(iv) A product precipitated is indicated by the sign ($\downarrow$) or (s).

(v) A gas evolved is shown by the sign ($\uparrow$) or (g).

(vi) Reversible reactions are indicated by using a double headed arrow ($\rightleftharpoons$).

1-5 ATOMIC MASS

The atoms of a particular element are identical in mass and their masses differ from the masses of atoms of other elements. Atoms are extremely small and it is impossible to determine their actual masses. However, by studying the mode in which atoms combine in hundreds of compounds, it is possible to obtain the relative masses of the atoms. A quantitative scale of relative atomic masses is developed by selecting one atom as a standard and comparing the mass of the other atoms to the standard. In the nineteenth century, firstly the atomic mass of hydrogen and then later the mass of oxygen were adopted as the standards. Since 1961, an atom of the isotope of carbon, carbon-12 has been the standard.

The atomic mass of an element is a numerical number which indicates how many times an atom of an element is heavier than one-twelfth mass of carbon-12 atom. For example, atomic mass of hydrogen is 1.008. This means that hydrogen atom is about one-twelfth as heavy as carbon-12 atom. One-twelfth of the mass of one atom of carbon-12 is known as *atomic mass unit* (amu). Carbon-12, an isotope of carbon, was assigned the atomic mass of 12.00 units in 1961. When the atomic mass of an element is expressed in grams, it is known as *gram atomic mass*. For example, the gram atomic mass of sodium is 23. Table 1-6 provides relative masses of the atoms.

Table 1-6 Atomic masses of some selected elements referred to $^{12}\text{C}=12.000$

<i>Elements</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Mass</i>
Aluminium	Al	13	27.0
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.9
Barium	Ba	66	137.34
Beryllium	Be	4	9.01
Bismuth	Bi	83	209.0
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.4
Caesium	Cs	55	132.9
Calcium	Ca	20	40.1
Carbon	C	6	12.0
Chlorine	Cl	17	35.5
Chromium	Cr	24	52.0
Cobalt	Co	27	58.93
Copper	Cu	29	63.55
Fluorine	F	9	19.0
Germanium	Ge	32	72.6
Gold	Au	79	197.0
Helium	He	2	4.0
Hydrogen	H	1	1.008
Iodine	I	53	126.90
Krypton	Kr	36	83.80
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Magnesium	Mg	12	24.3
Manganese	Mn	25	54.9
Mercury	Hg	80	200.6
Neon	Ne	10	20.2
Nickel	Ni	28	58.71
Nitrogen	N	7	14.0
Oxygen	O	8	16.0
Palladium	Pd	46	106.4
Phosphorus	P	15	31.0
Platinum	Pt	78	195.1
Potassium	K	19	39.1
Radium	Ra	88	226.0
Scandium	Sc	21	45.0
Silicon	Si	14	28.1
Silver	Ag	47	107.87
Sodium	Na	11	23.0
Sulphur	S	16	32.1
Tin	Sn	50	118.7
Titanium	Ti	22	47.90
Tungsten	W	74	183.85
Uranium	U	92	238.0
Zinc	Zn	30	65.4

1-6 MOLECULAR MASS

Molecular mass of a substance is the mass of one molecule of the substance in atomic mass units. Since molecules are composed of atoms, it follows that once the relative masses of the atoms are known it is possible to determine the relative mass of a molecule. For example, glucose molecule ($\text{C}_6\text{H}_{12}\text{O}_6$) has 6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms. Knowing the atomic masses of the elements, the molecular mass can be calculated.

The molecular mass of glucose is, thus 180.

$$6 \times \text{atomic mass of C} = 6 \times 12 = 72$$

$$12 \times \text{atomic mass of H} = 12 \times 1 = 12$$

$$6 \times \text{atomic mass of O} = 6 \times 16 = 96$$

$$\text{Total mass} = 180$$

When the molecular mass of a compound is expressed in grams, it is referred as the gram molecular mass.

1-7 THE MOLE

Each atom has mass. If we have a sample of an element, its mass must be the total of masses of the atoms that make it up. Now take two samples of the equal mass of two different elements. You will find unequal number of atoms in the two samples. Furthermore, if we take N_{Cl_2} chlorine molecules, N_{O_2} oxygen molecules and N_{NH_3} ammonia molecules, the masses of the three samples are,

$$\text{Mass of } \text{Cl}_2 = N_{\text{Cl}_2} \cdot m_{\text{Cl}_2}$$

$$\text{Mass of } \text{O}_2 = N_{\text{O}_2} \cdot m_{\text{O}_2}$$

$$\text{Mass of } \text{NH}_3 = N_{\text{NH}_3} \cdot m_{\text{NH}_3}$$

where m_{Cl_2} , m_{O_2} and m_{NH_3} are the masses of chlorine, oxygen and ammonia molecules respectively. The mass of each sample is proportional to its molecular mass. This proportionately applies to any collection of N molecules of any substance. We call any collection of 6.023×10^{23} particles, a mole (mol). This number of particles in a mole, (6.023×10^{23}) is called *Avogadro's number* (N). For example, 16g of oxygen (element) contains 6.023×10^{23} atoms; 32g of oxygen (compound) or 18g of water contains 6.023×10^{23} molecules. The term mole is also defined as the amount of any substance in grams that contains Avogadro's number, 6.023×10^{23} of particles.

Now it is evident that a mole of atoms or molecules is present in the atomic or molecular mass expressed in grams. This mass of any substance that contains a mole of particles is called *molar mass*.

Number of grams per mole or molar mass of an element (or substance) can be used:

(a) to find the number of moles of an element in a given mass:

$$\text{Number of moles} = \frac{\text{mass (in grams)}}{\text{molar mass}}$$

(b) to find the number of atoms of an element in a given mass:

$$\text{Number of atoms} = \frac{\text{mass (in grams)} \times N}{\text{molar mass}}$$

(c) to find the mass of a given number of moles of an element:

$$\begin{aligned} \text{mass (in grams)} \\ = \text{number of moles} \times \text{molar mass} \end{aligned}$$

Broadly, a mole is a unit of number (but not of size or mass) used for referring to atoms, molecules, ions, electrons, etc. The mole is equal to 6.023×10^{23} particles.

1-8 THE STATES OF MATTER

Matter exists in three states—gaseous, liquid and solid (Fig. 1-6). Matter in the solid state such as ice and steel have definite shape and definite volume. A liquid, such as water or oil occupies a definite volume but no specific shape. Liquids adapt to the shape of their containers. A gas has neither a definite shape nor volume and will occupy the entire container in which it is placed.

Solids have definite shape and volume because atoms and molecules are closely packed in a systematic way. Each atom and molecule has a fixed position in the solid and is not free to move.

Gases have neither a fixed volume nor a fixed shape. In gases, molecules are far apart from each other and are free to move due to weak intermolecular forces. A sample of gas fills any container of any size and shape.

The molecules in liquids are close to each other. This is why liquids have definite volume. But molecular arrangement in liquids is different from solids (Fig. 1-6). Molecules in a liquid are free to move. This is why liquids are fluid. We will now discuss the properties

We will now discuss the properties of gases and the laws that describe quantitatively the behaviour of gases.

1-9 PROPERTIES OF GASES

When a liquid is heated sufficiently it begins to boil and evaporate. This process is accompanied by a great change in volume. It has been observed experimentally that half a cupful of water at one atmospheric pressure and 100°C gives water vapour equal to 50-gallon oil drum. Since molecules in the gas phase are of the same size as they are in the liquid state, it follows that the distances between them in the gaseous state are much greater than in the liquid. All gases mix readily with one another to form completely homogeneous solutions. Air is such a solution. Gases are easy to compress.

Pressure

Evangelista Torricelli (1608-1647) demonstrated by a barometre that gases exert pressure. A simple barometre can be made by filling a

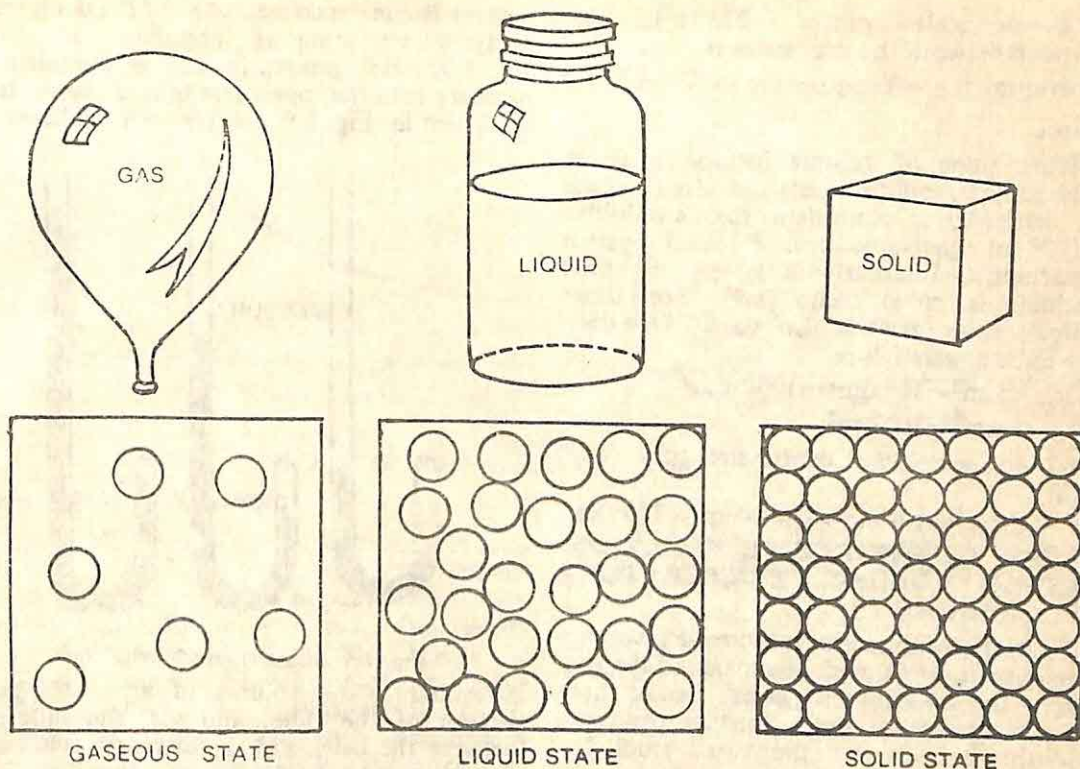


Fig. 1-6 The three states of matter

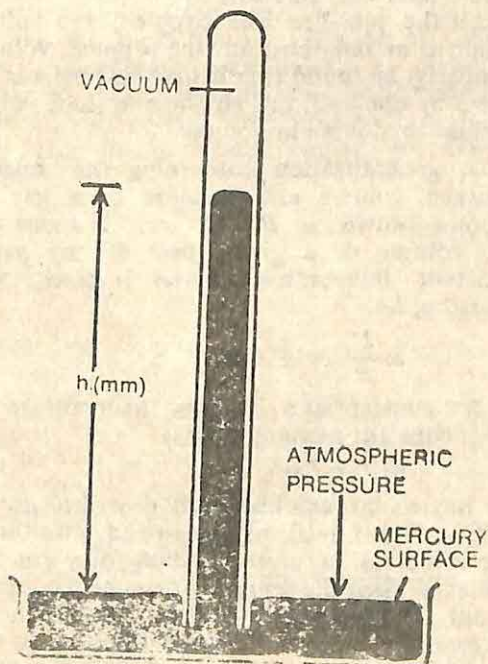


Fig. 1-7 The barometre. Pressure of atmosphere = pressure of mercury column = $h \text{ (mm)Hg} = 760 \text{ mm Hg}$ at standard atmospheric pressure and 273 K

glass tube open at one end with mercury and inverting the tube in a dish filled with mercury (Fig. 1-7). When the tube is placed in the dish, a small amount of mercury flows out of the tube. The rest of the mercury is prevented from running out of the tube by the pressure that the atmosphere exerts against the surface of the mercury in the dish.

The height of a column of mercury supported by the gas pressure is a measure of the pressure. The pressure is expressed in millimetres of mercury. One millimetre of mercury is called one 'torr' in honour of Torricelli. The normal pressure of the atmosphere at sea level supports a mercury column 760 mm high, so a pressure of 1 atmosphere (atm) is 760 torr.

Temperature

Gas expands when heated and contracts when cooled. The change in volume for any given gas sample is proportional to temperature. Temperature is measured in Celsius. The lowest point in the Celsius scale is 0°C . Another scale which avoids mathematical calculations of negative temperatures is the *Kelvin temperature scale* or *absolute temperature scale*. Zero on

the Kelvin scale equals -273.15°C , the conversion between the two scales is

$$\text{Temperature in K} = \text{Temperature in } ^{\circ}\text{C} + 273.15$$

Volume

Metric units of volume include the cubic centimetre (cc), millilitre (ml) and litre (l). One cubic centimetre is equivalent to one millilitre and 1000 ml equals one litre. S.I. unit (System Internationale—International system of units) of volume is cubic metre (m^3). Sometimes decimetre cube (dm^3) is also used. One decimetre cube equals 1 litre.

$$1 \text{ m}^3 = 10^3 \text{ dm}^3 = 1000 \text{ dm}^3$$

$$\text{or } 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

For smaller volumes, centimetre cube (cm^3) is used.

$$1 \text{ dm}^3 = 10^3 \text{ cm}^3 = 1000 \text{ cm}^3 = 1000 \text{ cc}$$

1-10 THE QUANTITATIVE RELATIONSHIPS OF VOLUME, TEMPERATURE AND PRESSURE

The four variables are pressure (P), volume (V), temperature (T) and the mass of the gas. To study the behaviour of gases, two of these four variables are kept constant and the relationship between the other two is studied.

1-10-1 BOYLE'S LAW

Robert Boyle (1627-1691) was an English scientist. He investigated the relationship between volume and pressure in a given mass of gas at constant temperature. Figure 1-8 illustrates, if the pressure of a gas sample increases, the volume will decrease; and if the pressure decreases, the volume will increase.

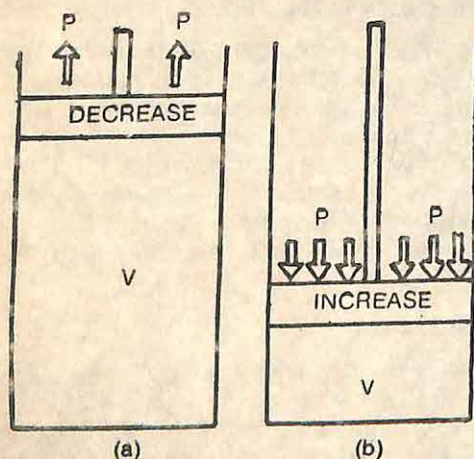


Fig. 1-8 (a) When the pressure decreases the volume increases, and (b) When the pressure increases the volume decreases

Robert Boyle experimented with the compressibility of air using an apparatus shown in Fig. 1-9. He poured increasing quantities of mercury into the open arm of a J-shaped tube as shown in Fig. 1-9. After each addition he

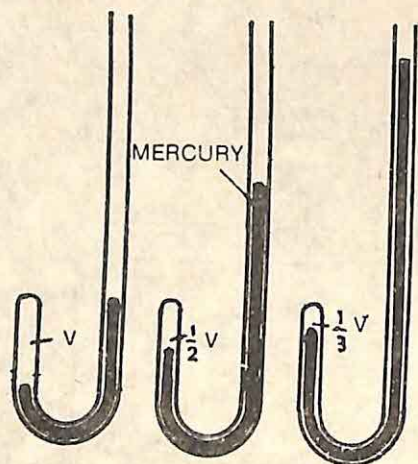


Fig. 1-9 Illustration of Boyle's law

measured (a) the volume of air in the closed section of the tube, and (b) the difference between the heights of the mercury columns in the two arms. Boyle observed that if the pressure on the enclosed air was doubled, the gas would have only one-half the original volume; and if the pressure was trippled, the volume dropped to one-third of the original volume. Similarly, he found that if the pressure was cut down by one half, the air in the tube would expand to double in volume.

A generalization concerning the relation between volume and pressure of a gas has become known as *Boyle's law*. It states that the volume of a given mass of any gas at constant temperature varies inversely with pressure, i.e.

$$V \propto \frac{1}{P} \text{ or } PV = k$$

(k is a constant at a constant temperature and for a constant amount of gas).

$$\text{or } P_1 V_1 = P_2 V_2$$

Boyle's law can be readily described graphically. Figure 1-10 represents the variation of the volume of a given amount of a gas with pressure when the temperature is held constant. From the graphs it is clear that as the gas pressure increases the volume decreases in such a way that the product of P and V remains constant.

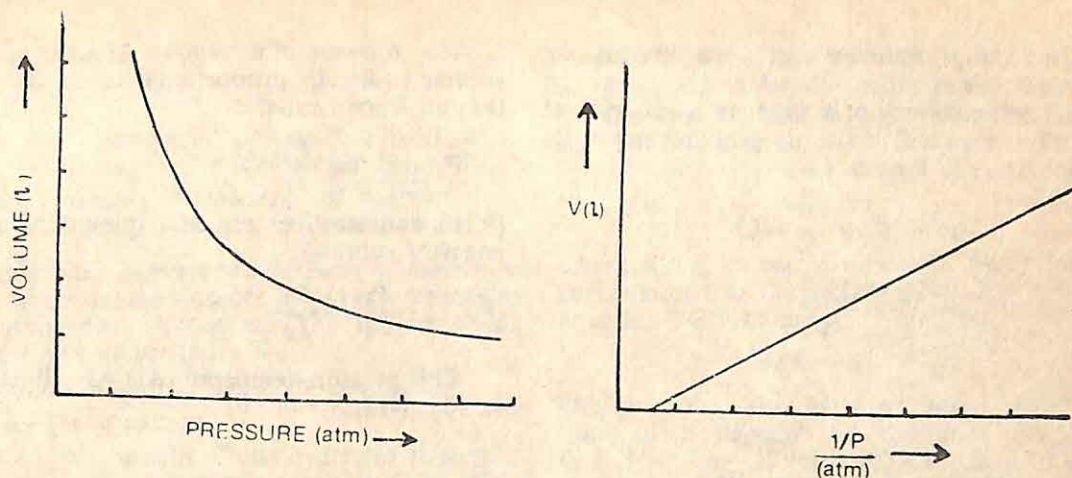


Fig. 1-10 Graphical representation of Boyle's law

1-10-2 CHARLES' LAW

J.A.C. Charles (1746—1833) was a French chemist. In 1787, he investigated the expansion of gases at constant pressure that occurs when the temperature is raised. His results were never published. In 1802, Joseph L. Gay-Lussac, also a French chemist, independently measured the expansion of gases, keeping the pressure constant, that occurs when the temperature is raised. He noted that when the temperature is increased the volume increases, and when the temperature is decreased the volume decreases. Both Charles and Gay-Lussac found that the variation of volume with temperature was linear at constant pressure. On extending the straight line plot between volume and temperature, it is found that the line cuts the temperature axis at

-273.15°C (Fig. 1-11). A similar observation was made for different gases. It seems as though all gas volumes would become zero at -273.15°C , but in fact gases liquefy or solidify long before this temperature is attained. The temperature -273.15°C was taken as the zero on a new temperature scale called the absolute temperature scale or the Kelvin scale. Accordingly the temperature on the Kelvin scale would be,

$$\text{Temperature in K} = \text{Temperature in } ^{\circ}\text{C} + 273.15$$

$$273.15 \text{ K} = 0^{\circ}\text{C}$$

On the Kelvin scale, the plot follows the expression,

$$V = kT$$

(where k is a constant for a given amount of gas)

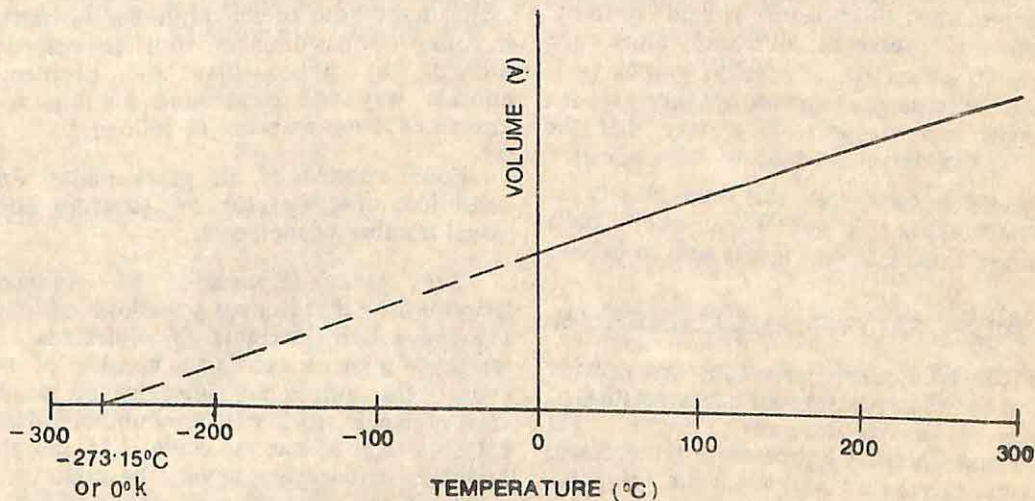


Fig. 1-11 A plot between volume and temperature at constant pressure

This proportionality has been known as Charles' law. Thus *Charles' law* can be stated: the volume of a fixed mass of gas at constant pressure is directly proportional to its temperature in Kelvin, i.e.

$$V \propto T \text{ or } \frac{V}{T} = k$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

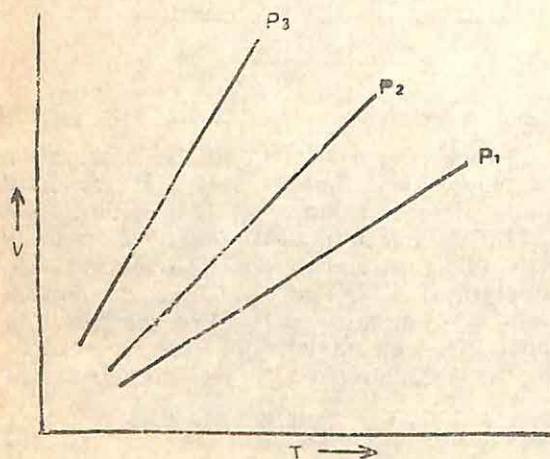


Fig. 1-12. Charles' law—plot of V (ml) vs. T (K) at constant pressure P (atm)

Charles' law can be readily described graphically. Fig. 1-12 represents the variation of the volume of a given amount of gas with temperature when the pressure is held constant. For different pressures different plots are obtained ($P_1 > P_2 > P_3$). From the graphs it is clear that as the gas temperature increases the volume also increases in such a way that the ratio of V/T remains constant.

All gases do not follow this trend closely at all temperatures. A gas which obeys both Boyle's law and Charles' law is said to behave ideally.

1-10-3 PRESSURE-TEMPERATURE LAW

In 1703, Guillaume Amontons investigated a relation between pressure and temperature of a sample of gas at constant volume. He observed that when the temperature is increased, the pressure increases; and when the temperature is decreased the pressure decreases. This relation can be stated as below:

The pressure of a sample of a gas of fixed volume is directly proportional to the temperature on Kelvin scale, i.e.,

$$P \propto T \text{ or } \frac{P}{T} = k$$

(k is a constant for a given amount of gas at constant volume)

$$\text{or } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This pressure-temperature law is illustrated in Fig. 1-13.

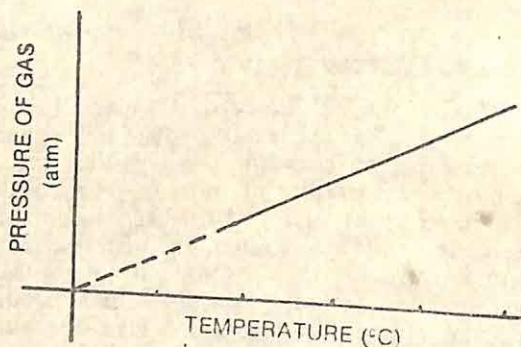


Fig. 1-13 The relation between the pressure and the temperature of a gas

1-10-4 AVOGADRO'S HYPOTHESIS

Amedeo Avogadro (1776-1856) was an Italian scientist. He also believed in the earlier hypothesis of equal number of particles in equal volumes of gases, but he solved the difficulty by approaching the problem in another way and enunciated his famous law, known as *Avogadro's law* as follows:

Equal volumes of all gases under similar conditions of temperature and pressure, contain equal number of molecules.

The great importance of Avogadro's hypothesis is that it gives a method of obtaining the relative weights of molecules. The weight of a gas sample is the number of molecules in the sample multiplied by the weight of each molecule, i.e., $\text{weight} = \text{number of molecules} \times \text{weight of one molecule}$. If samples of hydrogen and oxygen having the same volume, temperature and pressure are weighed, the sample weights have the ratio,

$\left(\frac{\text{weight of hydrogen}}{\text{weight of oxygen}} \right)$ same V, T, P

$$= \frac{\text{number of molecules of hydrogen} \times \text{weight of one hydrogen molecule}}{\text{number of molecules of oxygen} \times \text{weight of one oxygen molecule}}$$

But since the number of hydrogen molecules is the same as the number of oxygen molecules by Avogadro's hypothesis, the number terms cancel and we are left with,

$$\left(\frac{\text{weight of hydrogen}}{\text{weight of oxygen}} \right) \text{ same } V, T, P$$

$$= \frac{\text{weight of one hydrogen molecule}}{\text{weight of one oxygen molecule}}$$

1-10-5 IDEAL GAS LAW

The laws of Boyle and Charles can be combined to obtain a more general law for the behaviour of gases. Let P_1, V_1, T_1 and P_2, V_2, T_2 be the pressure, volume and temperature in states 1 and 2 respectively of any definite quantity of a gas. This can be done in two steps :

Step 1 : At constant temperature T_1 , when the pressure P_1 is changed to P_2 , the volume V_1 changes to V_2 . According to Boyle's law :

$$P_1 V_1 = P_2 V_2$$

or
$$V_2 = \frac{P_1 V_1}{P_2} \quad (1-1)$$

Step 2 : At constant pressure P_2 , when the temperature T_1 is changed to T_2 , the volume V_2 changes to V_3 . According to Charles' law :

$$\frac{V_2}{T_1} = \frac{V_3}{T_2}$$

or
$$V_3 = \frac{T_2 V_2}{T_1} \quad (1-2)$$

From equations (1-1) and (1-2)

$$\frac{P_1 V_1}{P_2} = \frac{T_2 V_3}{T_1}$$

or
$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_3}{T_2} = \text{constant, } k$$

In general
$$\frac{PV}{T} = k$$

Thus, for a given amount of gas $\frac{PV}{T}$ is constant. The numerical value of k depends

on the amount of the gas but is independent of the nature of gas. For one mole of the gas, the constant is referred to as the *molar gas constant* and is denoted by R .

Therefore,
$$\frac{PV}{T} = R \quad (1-3)$$

where R is a universal constant for all gases and is known as the *gas constant*. For n moles, equation 1-3 becomes

$$PV = nRT$$

This is called the *ideal gas law*. Numerical value of R depends on the units used for P, T, V and n . If volume is expressed in litres, pressure in atmospheres, temperature in Kelvin and n as the number of moles, then the unit of R will be,

$$R = \frac{PV}{nT} = \frac{\text{atm litre}}{\text{mole Kelvin}}$$

$$= \text{atm litre per degree Kelvin per mole}$$

There are other ways also of expressing the unit of R .

Now the value of R can be calculated from the fact that 1 mole of every gas at STP occupies a volume of 22.4 litres.

1-11 STP AND MOLAR VOLUME

Standard temperature and pressure is abbreviated as STP. What volume does 1 mole of a gas occupy at STP? This can be easily calculated by substituting,

$$P = 1.00 \text{ atm} \quad T = 273 \text{ K}$$

$$n = 1.00 \text{ mole}$$

$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

in the relation $V = \frac{nRT}{P}$, we get

$$V = \frac{1 \times 0.0821 \times 273}{1}$$

$$= 22.4 \text{ litres}$$

Thus, 1 mole of an ideal gas will occupy a volume of 22.4 litres at STP. The value 22.4 litres per mole is called the *molar volume* of a gas and is valid at STP. Thus

$$R = \frac{PV}{nT} = \frac{1 \times 22.4}{1 \times 273}$$

$$= 0.0821 \text{ litre-atmosphere per degree Kelvin per mole}$$

In S.I. units

$$1 \text{ atmosphere} = 1.01325 \times 10^5 \text{ Nm}^{-2}$$

$$1 \text{ litre} = 10^{-3} \text{ m}^3 = 1 \text{ dm}^3$$

Therefore $P = 1.01325 \times 10^5 \text{ Nm}^{-2}$

$$V = 0.0224 \text{ m}^3$$

$$T = 273 \text{ K}$$

and

$$R = \frac{1.01325 \times 10^5 \times 0.0224}{273}$$

$$= 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

(joules per degree Kelvin per mole)

Since $1 \text{ joule} = 10^7 \text{ ergs}$

and $1 \text{ calorie} = 4.184 \text{ joules}$

Therefore $R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$

$$R = \frac{8.314}{4.184}$$

$$= 1.987 \text{ calories K}^{-1} \text{ mol}^{-1}$$

SOLVED NUMERICALS

1-1. What is the molecular mass of $\text{CH}_3\text{CO}_2\text{H}$?

Solution. The formula can be rewritten as $\text{C}_2\text{H}_4\text{O}_2$. The mass of the molecule is the total of the masses of two carbon atoms, four hydrogen atoms and two oxygen atoms.

Molecular mass in amu

$$= 2 \times 12 + 4 \times 1 + 2 \times 16$$

$$= 24 + 4 + 32$$

$$= 60 \text{ amu}$$

1-2. What is the mass in grams of 0.750 mol of O_2 ?

Solution.

$$\text{Molecular mass of } \text{O}_2 = 2 \times 16 = 32 \text{ amu}$$

The mass of 1 mol of O_2 is, therefore, 32 g.

$$\text{Mass of } 0.750 \text{ mol} = 0.750 \times 32$$

$$= 24.0 \text{ g}$$

1-3. How many moles are present in 14.0 g of C_2H_4 ?

Solution.

$$\text{Molecular mass of } \text{C}_2\text{H}_4 = 2 \times 12 + 4 \times 1$$

$$= 24 + 4 = 28 \text{ amu}$$

The mass of 1 mol of C_2H_4 is, therefore, 28.0 g.

$$\text{Number of moles} = \frac{14.0}{28.0} = 0.50$$

1-4. Calculate the number of atoms in $1.0 \times 10^{-3} \text{ g}$ of aluminium.

Solution.

$$\text{One g atomic mass of aluminium} = 26.98 \text{ g}$$

$$1 \text{ g atomic mass} = 1 \text{ mol}$$

$$= 6.023 \times 10^{23} \text{ atoms}$$

Therefore, the number of atoms of aluminium in $1.0 \times 10^{-3} \text{ g}$

$$= \frac{6.023 \times 10^{23} \times 10^{-3}}{26.98}$$

$$= 2.23 \times 10^{19}$$

1-5. Convert a pressure of 550 torr into atmospheres.

Solution. $1 \text{ atmosphere} = 760 \text{ torr}$

$$\text{Therefore, } 550 \text{ torr} = \frac{550}{760} = 0.724 \text{ atm}$$

1-6. A gas occupies 225 dm^3 volume at 3.25 atm and 300 K . What pressure is needed to reduce its volume to 160 dm^3 at 300 K .

Solution. Initially $P_1 = 3.25 \text{ atm}$

$$V_1 = 225 \text{ dm}^3 \text{ (litres)}$$

$$\text{Finally } P_2 = ?$$

$$V_2 = 160 \text{ dm}^3$$

Since temperature of the gas remains constant, we can use Boyle's law.

$$P_1 V_1 = P_2 V_2$$

$$\text{Substituting : } 3.25 \times 225 = P_2 \times 160$$

$$P_2 = \frac{3.25 \times 225}{160} = 5.18 \text{ atm}$$

1-7. A gas in a cylinder is heated at a constant pressure of 760 mm Hg from 303 K to 643 K . If the gas initially has a volume of 3.00 dm^3 , find the final volume.

Solution. Initially : $V_1 = 3.00 \text{ dm}^3$

$$T_1 = 303 \text{ K}$$

$$\text{Finally : } V_2 = ?$$

$$T_2 = 643 \text{ K}$$

Since pressure of the gas remains constant, we can use Charles' law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\text{Substituting, } \frac{3}{303} = \frac{V_2}{643}$$

$$V_2 = \frac{3 \times 643}{303}$$

$$= 6.37 \text{ dm}^3 \text{ (litres)}$$

or

1-8. A gas occupies a volume of 3.60 dm^3 at 298 K and 2.49 atm . How many moles of gas are in the sample.

Solution. $V = 3.60 \text{ dm}^3$; $T = 298 \text{ K}$
 $P = 2.49 \text{ atm}$; $n = ?$
 $R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$

Using ideal gas law,

$$PV = nRT$$

$$n = \frac{PV}{RT} = \frac{2.49 \times 3.60}{0.0821 \times 298}$$

$$= 0.367 \text{ mol}$$

1-9. Consider a 325 litres sample of gas at 298 K and 750 mm of Hg . If the volume is changed to 315 litres and the pressure to 760 mm of Hg , what is the final temperature of the gas?

Solution. $P_1 = 750 \text{ mm}$, $P_2 = 760 \text{ mm}$
 $V_1 = 325 \text{ litres}$ $V_2 = 315 \text{ litres}$
 $T_1 = 298 \text{ K}$ $T_2 = ?$

According to the gas law,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Substituting : } \frac{750 \times 325}{298} = \frac{760 \times 315}{T_2}$$

or

$$T_2 = \frac{760 \times 315 \times 298}{750 \times 325}$$

$$= 293 \text{ K}$$

1-10. A gas occupies 28.3 litres at S.T.P. . How many moles of gas are in this volume?

Solution.

Volume of 1 mol of gas at $\text{STP} = 22.4 \text{ litres}$

Therefore, number of moles

$$= \frac{28.3}{22.4}$$

$$= 1.26$$

KEY TERMS

- 1-1 Matter.** Anything that occupies space and has weight.
- 1-2 Atom.** The smallest particles of an element which can take part in a chemical reaction.
- 1-3 Element.** A substance composed of only one type of atoms.
- 1-4 Molecule.** The smallest particle of an element or a compound which can normally exist separately.
- 1-5 Atomic Mass.** The mass of one atom of the element.
- 1-6 Atomic Mass Unit (amu).** One twelfth of the mass of one atom of the isotope of carbon, carbon-12.
- 1-7 Relative Atomic Mass.** The number of times an atom of an element is heavier than one-twelfth of the mass of a carbon-12 atom.
- 1-8 Molecular Mass.** The number of times a molecule of the compound is heavier than one-twelfth of the mass of a carbon-12 atom.
- 1-9 Mole.** Molecular mass expressed in gram is equivalent to 1 mole . A mole contains 6.023×10^{23} molecules (Avogadro's number).
- 1-10 Symbol.** A brief representation of the name of an element.
- 1-11 Formula.** A brief representation of the composition of a compound.
- 1-12 Chemical equation.** Represents a chemical reaction with the help of symbols and formulae of the substances involved.
- 1-13 Boyle's law.** The volume of a given mass of a gas at constant temperature varies inversely with the pressure.
- 1-14 Charles' law.** At constant pressure the volume of a given mass of a gas is directly proportional to its absolute temperature.
- 1-15 Absolute temperature.** Celsius temperature increased by 273.15
 $T = 273.15 + t^\circ\text{C}$.

1-16 Ideal Gas law. $PV=nRT$

(P -pressure, V -volume, T -absolute temperature (Kelvin scale), n -number of moles of gas, R -gas constant).

1-17 Gas Constant (R). The value of R in different units is as follows :

$$R=0.0821 \text{ litre atmosphere per degree Kelvin per mole}$$

$$R=8.314 \text{ NmK}^{-1} \text{ mol}^{-1}$$

$$R=8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$R=8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$$

$$R=1.987 \text{ calories K}^{-1} \text{ mol}^{-1}$$

1-18 Standard Temperature and Pressure (STP). Standard temperature (T) is 273.15K . Standard pressure (P) is $760 \text{ torr}=1 \text{ atm}$.**1-19 Gram Molecular Volume.** The volume occupied by one mole of a gas at STP= $22.4 \text{ litres}=22.4 \text{ dm}^3$.**1-20 Avogadro's law.** Equal volumes of gases contain same number of molecules at the same temperature and pressure.**UNIT THROUGH EXERCISES**

1-1 Choose the true statements of the following :

- (i) Anything having mass and occupying space is called matter.
 - (ii) Electrons and photons of light are examples of matter.
 - (iii) Different elements have atoms that differ in mass and size.
 - (iv) Co is the element cobalt and CO is the compound carbon monoxide.
 - (v) The formula of calcium hydroxide is CaOH_2 and not $\text{Ca}(\text{OH})_2$.
 - (vi) $\text{CH}_4 + \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ is a balanced equation.
 - (vii) Two elements sometimes form more than one compound.
 - (viii) Temperature in $^\circ\text{C}$ = Temperature in K $+ 273.15$.
 - (ix) $1 \text{ atm}=760 \text{ mm of mercury}=760 \text{ torr}$.
 $1 \text{ litre}=10^{-3} \text{ m}^3=1 \text{ dm}^3$
 - (x) At STP the volume of 1 mole of every gas equals 22400 millilitres.
- Ans.** (i), (iii), (iv), (vii), (ix) and (x) are true statements.

1-2 Name the suitable term to which the following statements are related.

- (i) A shorthand representation of an element.
- (ii) The fundamental unit of an element.

(iii) A shorthand representation of a compound.

(iv) The fundamental unit of a compound.

(v) Avogadro's number of particles.

(vi) Substances that cannot be separated into simpler substances.

(vii) Substances that have properties different from the constituent element.

(viii) Constituents are present in any proportion.

(ix) Represents an actual chemical reaction with the help of symbols and formulae.

(x) One-twelfth of the mass of one atom of carbon-12.

Ans. (i) Symbol, (ii) Atom, (iii) Formula, (iv) Molecule, (v) Mole, (vi) Elements, (vii) Compound, (viii) Mixture, (ix) Chemical equation, (x) Atomic mass unit.

1-3 Mention the scientific laws for the following statements :

(i) At constant pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature.

(ii) Equal volumes of all gases under the same conditions of temperature and pressure contain same number of molecules.

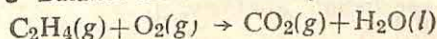
- (iii) At constant temperature, the volume of a given mass of a gas is inversely proportional to the pressure.
- (iv) The pressure of a sample of a gas of fixed volume is directly proportional to the absolute temperature.
- (v) Matter is neither created nor destroyed in a chemical process.
- (vi) When two or more elements combine to form a compound, the ratio of the masses of the elements is always the same.

Ans. (i) Charles' law (ii) Avogadro's law
 (iii) Boyle's law
 (iv) Pressure-temperature law
 (v) Law of conservation of matter
 (vi) Law of definite proportion

1-4 In the formula $2\text{Fe}_2(\text{SO}_4)_3$, how many iron, sulphur, oxygen and sulphate units are there?

Ans. (a) Iron atoms $= 2 \times 2 = 4$
 (b) Sulphur atoms $= 2 \times 3 \times 1 = 6$
 (c) Oxygen atoms $= 2 \times 3 \times 4 = 24$
 (d) Sulphate ions $= 2 \times 3 = 6$

1-5 Balance the skeleton equation



and answer the following questions.

- (a) How many moles of oxygen are needed to produce 2 moles of CO_2 ?
- (b) How many grams of C_2H_4 are required to produce 2 moles of water?

Ans. $\text{C}_2\text{H}_4(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 (a) 3 moles, (b) 28 g

1-6 (a) How will you indicate the following effects in a chemical equation?

- (i) Evolution of gas
- (ii) Formation of a precipitate
- (iii) Reactant is heated to give products
- (iv) Exothermic reaction
- (v) Endothermic reaction

Ans. (i) $\uparrow$ (ii) $\downarrow$ (iii) $\xrightarrow{\Delta}$
 (iv) '+heat' with products
 (v) '-heat' with products

(b) What are the symbols for the following physical states of reactants and products in chemical equations?

- (i) Gaseous state
- (ii) Solid state
- (iii) Liquid state
- (iv) Aqueous solution (solution made in water)

Ans. (i) (g), (ii) (s), (iii) (l), (iv) (aq).

Multiple Choice Questions

1-7 Pick up the suitable choice:

1. The formula of copper carbonate is (Cu_2CO_3 , $\text{Cu}(\text{CO}_3)_2$, CuCO_3).
2. H_2S is (monoatomic, diatomic, triatomic, tetratomic) molecule.
3. The formula of nitrate ion is (NO_3^- , NO_2^- , NO_3^{2-}).
4. Brass, milk and paint are examples of a (mixture, compound, element).
5. At constant pressure $\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$, is the mathematical statement of (Boyle's law, Charles' law, Graham's law).
6. $20 \text{ dm}^3 =$ (40 litres, 20 litres, 10 litres).
7. 64 grams of $\text{O}_2 =$ (2 moles, 4 moles, 6 moles).
8. $38 \text{ cm Hg} =$ (1 atm, 0.5 atm, 2 atm).
9. $-18^\circ\text{C} =$ (291 K, 283 K, 255 K).
10. Symbol for calcium is (C, Cl, Ca, Cu).

Ans. 1. CuCO_3 , 2. triatomic, 3. NO_3^- , 4. mixture, 5. Charles' law, 6. 20 litres, 7. 2 moles, 8. 0.5 atm, 9. 255 K, 10. Ca.

1-8 Fill in the blanks:

- (a) An element is composed of only one type of
- (b) Compounds are substances composed of two or more united chemically in a definite proportion by mass.
- (c) is the smallest particle of a substance (element or compound) which has properties of that substance and can exist freely.
- (d) One-twelfth of the mass of one atom of carbon-12 is known as
- (e) Equal volumes of different gases at the same temperature and pressure contain number of molecules.

- (f) The actual number of molecules in one gram-mole of a gas is known as.....
- (g) The formula of sodium sulphate is
- (h) Kelvin and celsius scales are related as
- (i) $\frac{P_1 V_1}{T_1} = \dots\dots\dots$

(j) Sodium reacts with water to form hydrogen and.....

- Ans. (a) atoms, (b) elements, (c) molecule, (d) amu, (e) same, (f) Avogadro's number, (g) Na_2SO_4 , (h) $K = 273.15 + t^\circ\text{C}$, (i) $\frac{P_2 V_2}{T_2}$, (j) sodium hydroxide

1-9 Complete the sentences in column A with suitable choice given in column B.

Column A

- (i) A mixture will be called homogeneous
- (ii) The properties of a compound are quite different
- (iii) Each element is composed of
- (iv) Molecule formed from the same kind of atoms
- (v) At constant volume, pressure of a given quantity of a gas
- (vi) Molecules formed by the union of different kinds of atoms
- (vii) One mole of a gas is equal to
- (viii) In equation $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- (ix) Free movement of molecules in gaseous state
- (x) At constant pressure, the volume occupied by a definite amount of a gas

Column B

- (i) extremely small particles called atoms.
- (ii) varies directly with the absolute temperature.
- (iii) if the composition is same throughout.
- (iv) from the properties of the constituent elements.
- (v) is a molecule of an element.
- (vi) is a molecule of a compound.
- (vii) 22.4 litres at STP.
- (viii) is directly proportional to absolute temperature.
- (ix) results into homogeneity.
- (x) 2 moles of water are obtained from 1 mole of methane.

REVIEW QUESTIONS

1-1 Define the word 'matter' and list five examples.

1-2 Distinguish between an element, a mixture and a compound.

1-3 What is symbol? Give examples.

1-4 The most important elements that compose the foods we eat are C, H, O, N, P, S, Ca, K, Cl, Na, Mg, and Fe. Give the names of these elements.

1-5 Identify each of the following substances as mixture, compounds or elements:

- | | | |
|------------|-----------|-------------|
| (a) wood | (b) sugar | (c) brass |
| (d) copper | (e) iron | (f) rust |
| (g) water | (h) milk | (i) glucose |
| (j) silver | (k) salt | (l) urea |

1-6 Distinguish between a symbol and a formula.

1-7 Write the formulae for water, carbon dioxide, sulphuric acid, sodium hydroxide and benzene.

1-8 Define the 'molecule'. How does a monoatomic molecule differ from a diatomic molecule?

1-9 Identify monoatomic, diatomic, triatomic and tetraatomic molecules from the following:

- (a) NaCl (b) Xe (c) CO_2 (d) NH_3
 (e) P_4 (f) H_2O_2 (g) O_3 (h) I_2 (i) He
 (j) C_2H_2 (k) Ne

1-10 Give statements for the followings :

- (a) law of conservation of energy
(b) law of constant composition.

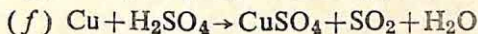
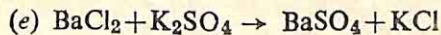
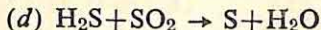
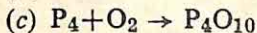
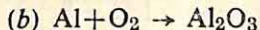
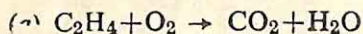
1-11 The elements that are needed in our diets in very small amounts are chromium, cobalt, copper, iodine, manganese, molybdenum, zinc, fluorine and tin. Give the symbols of these elements.

1-12 List four assumptions of Dalton's atomic theory.

1-13 Give the names and molecular formulae for the elements that occur naturally in the form of diatomic molecules.

1-14 (a) What is a chemical equation ?
(b) What is a balanced equation ?

1-15 Balance the following equations :



1-16 Give the correct formulae for the compounds formed by combination of the positive and negative ions given in the following table :

	OH^-	Cl^-	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}
Ag^+					
Ba^{2+}					
Fe^{3+}					
Cu^{2+}					
Na^+					
Al^{3+}					

1-17 Describe the following terms :

- (a) Atomic mass (b) Molecular mass
(c) Mole (d) Avogadro's number

1-18 Find the molecular mass of,

- (a) N_2O_4 (b) H_2NOH (c) C_2H_6O
(d) Fe_2O_3 (e) H_2SO_4 .

1-19 Give the formula of the following compounds :

- (a) Barium chloride
(b) Sodium carbonate
(c) Zinc phosphate
(d) Ammonium sulphate
(e) Calcium phosphate
(f) Silver bromide

1-20 Define the following :

- (a) Pressure (b) Force (c) STP
(d) Absolute zero (e) Ideal gas

1-21 What is torr ? What is an atmosphere? State the relation between these two units in the form of a factor.

1-22 Give a statement for each of the following gas laws :

- (a) Boyle's law
(b) Charles' law
(c) Pressure-temperature law

1-23 For a mole of ideal gas, plot :

- (a) A graph of P vs. T at constant volume.
(b) A graph of PV vs. P at constant temperature.
(c) A graph of PV vs. V at constant temperature.

1-24 Derive mathematical relationship between pressure, volume and temperature of a given mass of a gas.

1-25 What is the significance of 22.4 dm^3 of a gas ?

UNSOLVED NUMERICALS

1-1 How many ammonia molecules are present in 0.060 mol of NH_3 ?

Ans. 3.6×10^{22}

1-2 What is the mass, in grams, of 1.00×10^{21} water molecules ?

Ans. $2.99 \times 10^{-2} \text{ g}$

1-3 Determine the number of moles in each sample of elements given below :

- (a) 10.5 g iron nails
(b) 56.0 g sample of nitrogen (N_2)
(c) 720 g sample of sulphur.

Ans. (a) 0.188 moles (b) 2.00 moles of N_2
or 4.00 moles of N (c) 22.5 moles

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- 1-4 How many oxygen atoms are present in 0.0150 mol of O_2 ? **Ans.** 1.8×10^{22}
- 1-5 Calculate the number of atoms in a 37.9 g sample of aluminium foil.
Ans. 8.46×10^{23}
- 1-6 Determine the mass, in grams, of the following :
(a) 2.7 moles of Ag
(b) 6.54×10^{-5} moles of Na
Ans. (a) 291 g (b) 1.50×10^{-3} g
- 1-7 How many torr are present in 1.25 atm?
Ans. 950 torr
- 1-8 A gas sample exerts a pressure of 1026 torr. What is the pressure in atmosphere?
Ans. 1.35 atm
- 1-9 A gas occupies 25.0 ml at 298K and 745 torr. What volume would it occupy at STP?
Ans. 22.5 ml
- 1-10 A gas occupies 45.6 ml at 240 torr and 291K. What volume will it occupy at 598 torr and 291K.
Ans. 18.3 ml
- 1-11 A gas occupies 25.0 ml at 298K and 745 torr. What is its volume at 423K and 745 torr.
Ans. 35.5 ml.
- 1-12 A sample of air occupying 4.50 dm³ at 328K and 958 torr is cooled to 258K and its pressure is reduced to 720 torr. What is the new volume of the sample?
Ans. 4.84 dm³

UNIT 2

Substances—Their Separation and Purification



Robert Brown
(1773-1858)

Robert Brown established the concept of the continuous motion of minute particles suspended in fluid. This type of motion is called 'Brownian motion' after the name of the scientist. It is a property of both organic and inorganic matter.

Learning Objectives

At the completion of this unit, you should be able to :

1. Define mixture and compound. Give examples of each.
2. Define true solution, colloidal solution and suspension with examples.
3. Differentiate between the above three types of solutions.
4. Explain Tyndall effect and Brownian movement with illustrations.
5. Explain the principle and working of different types of methods used in separating constituents of a mixture.
6. Suggest method/methods to separate the constituents of any given mixture
7. Perform tests to find out the purity of substances.

2-1 INTRODUCTION

A pure substance is defined as any kind of matter of which all samples have identical composition and identical properties. For example, all samples of methyl alcohol contain exactly the same proportion of carbon, hydrogen and oxygen, regardless of the sources of samples. All samples have the same melting and boiling points. Pure substances may be

elements or compounds : when elements or compounds are mixed, a mixture is formed. The various constituents of a mixture have different physical properties. This difference in their physical properties is utilized to separate them from a mixture. The constituents of a mixture can be separated by physical methods like sedimentation and decantation, filtration, evaporation, sublimation, distillation, crystallization, magnet, separating funnel, etc.

2-2 MIXTURE AND COMPOUND

Both mixture and compound have been introduced in Unit 1. The composition of a mixture can be varied widely. A large number of mixtures of salt and sugar can be made by varying the amounts of these two substances. The important characteristics of a mixture are : (i) their composition can be varied, and (ii) each component of the mixture retains its own properties. Air, sea water, ink, gun powder, baking powder, smoke, milk, vinegar, honey, blood and urine are examples of mixture. A compound cannot be separated into its constituents by physical methods. Compounds can be decomposed into their constituent elements (Fig. 1-1). The physical and chemical properties of a compound are different from the properties of its constituent elements. Now we shall discuss various methods employed to separate the constituents of a mixture and of purifying them.

2-3 SEPARATION OF CONSTITUENTS FROM A MIXTURE

Mixtures are of two types—homogeneous and heterogeneous. These can exist in any of the three states (solid, liquid or gas). Table 2-2 lists various types of mixture.

There are different methods which can be used for the separation of constituents of a mixture. The choice of the method depends upon the nature of the constituents present in the mixture. The melting point, boiling point, solubility, etc. are considered to be the basis of their separation. Some of the common methods used for this purpose are explained below.

2-3-1. SEDIMENTATION AND DECAN-TATION

When sand is added to water in a beaker it settles down at the bottom of the beaker (Fig. 2-1). This is called *sedimentation*. The supernatant liquid is carefully poured into another beaker with the help of a glass rod as shown in Fig. 2-2. During this process the sand at the bottom is not disturbed. This process is called *decantation*. The process of sedimentation followed by decantation is employed to separate a mixture of a liquid component and an insoluble solid component heavier than the liquid component.

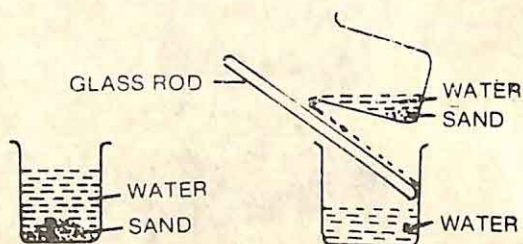


Fig. 2-1 Sedimentation

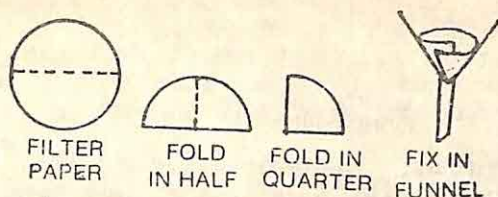
Fig. 2-2 Separation by decantation

2-3-1. FILTRATION

This method is employed to separate an insoluble component from a liquid. The mixture of insoluble component and the liquid is poured on a filter paper fixed in a funnel (Fig. 2-3). The residue (insoluble component) will remain on the filter paper and the clear liquid will pass through the filter paper and is collected in a beaker. The liquid thus collected is called *filtrate* (Fig. 2-3). This process is called *filtration*. The precipitate formed in a chemical reaction is separated by filtration.

Table 2-2. Examples of different types of mixtures

Types of mixture	Homogeneous	Heterogeneous
Gas in gas	Air	—
Gas in liquid	Aerated water ($\text{CO}_2 + \text{H}_2\text{O}$)	—
Gas in solid	Hydrogen in palladium	—
Liquid in gas	Mositure in air when we have mist	—
Liquid in solid	Jellies	—
Liquid in liquid	Alcohol in water	Oil + water
Solid in gas	—	Smoke (carbon in air)
Solid in solid	Alloys (brass, bronze)	Gun powder (potassium nitrate + sulphur + charcoal)
Solid in liquid	Salt in water	Sand + water



Folding and correct fixing of the filter paper on funnel.

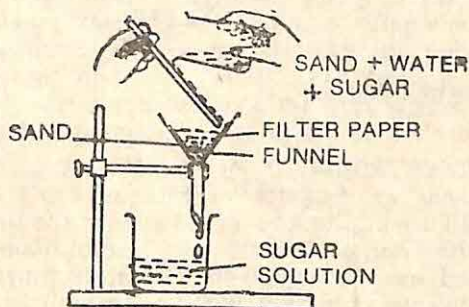


Fig. 2-3 Separation by filtration.

This method could be used to separate the following mixtures.

(i) *Sugar and Sand*. Sugar is soluble in water. On filtration sand will get collected on the filter paper. Sugar solution will pass through filter paper. From this solution sugar will crystallize out on concentrating the solution.

(ii) *Sugar and Sulphur*. Sugar is soluble in water whereas sulphur is insoluble in water.

(iii) *Charcoal powder and Sulphur*. Sulphur is soluble in carbon disulphide whereas charcoal powder is insoluble in carbon disulphide.

Thus by making use of the preferential solubility of one substance in a specific solvent, one can separate the two constituents of the mixture.

2-3-3. EVAPORATION

This method is employed for a mixture of miscible components and if the desired com-

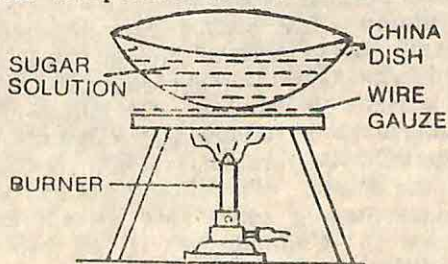
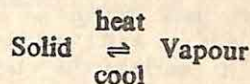


Fig. 2-4. Evaporation

ponent is non-volatile. When a mixture of sugar and water is heated slowly in a china dish on a wire gauge as shown in Fig. 2-4, water evaporates and passes into the atmosphere. The residue (sugar) left in china dish can be collected. This method is called *evaporation*.

2-3-4. SUBLIMATION

This method is employed to separate a volatile component (like naphthalene, iodine, ammonium chloride, camphor, etc) from a mixture with non-volatile component. On heating, the volatile component in a mixture changes directly into vapours without liquefying. The vapours become solid on cooling. This process is called *sublimation*.



In a mixture of *ammonium chloride and sodium chloride*, ammonium chloride is a volatile component. This mixture is taken in a china dish and is covered with an inverted funnel as shown in Fig. 2-5. The stem of the funnel is plugged with cotton wool. The solid deposited on the inner side of the funnel is collected. The non-volatile sodium chloride is left in the dish.

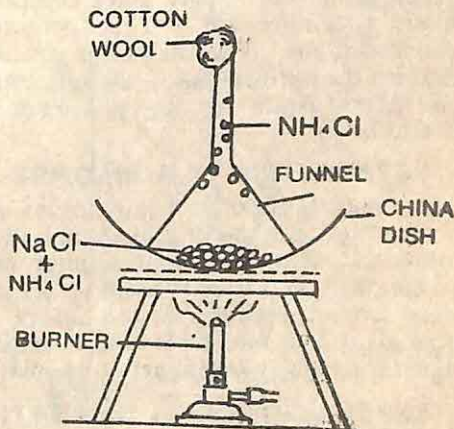


Fig. 2-5. Sublimation

2-3-5. DISTILLATION

Distillation is a process where a liquid on heating changes into vapours and then vapours on cooling convert into liquid. This method is employed to separate a mixture when both components are liquids or one is a soluble solid and the other is a liquid. *Water and*

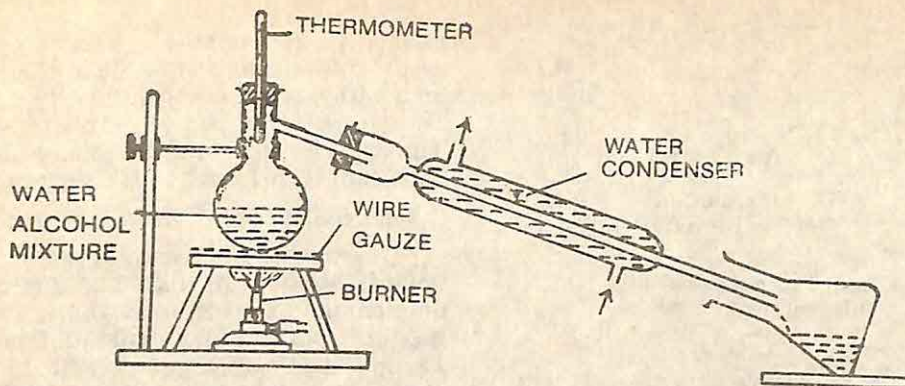


Fig. 2-6. Separation of a mixture by distillation

alcohol are completely miscible. Alcohol is a volatile component. The mixture is taken in a round bottom flask which is fitted with a thermometer and a water condenser as shown in Fig. 2-6. On heating, the alcohol vapours pass through the condensing unit where these are cooled and collected in a receiver. Water remains as residue in the flask. A mixture of salt and water can also be separated by this method.

2-3-6. CRYSTALLIZATION

Solid substances are more soluble in hot water than in cold water or some other solvent depending upon the nature of the substance. Therefore, if we cool down a saturated solution of a substance, it will slowly start separating and finally crystallize out. This method is called *crystallization*. This method is generally employed for the purification of the substances. Crystals that separate on cooling are filtered, washed and dried.

2-3-7. SEPARATION BY A MAGNET

When a magnet is put in a mixture of *iron filings and sulphur*, the iron filings stick to the magnet and get separated from sulphur (Fig. 1-3). This method can be used to separate iron filings from a mixture of *iron filings and carbon powder*. This method is used to separate the magnetically active component of a mixture.

2-3-8. SEPARATION BY A SEPARATING FUNNEL

A mixture of two immiscible liquids can be separated by this method. Oil and water do not mix but form separate layers. When these two immiscible liquids are taken in a separating funnel (Fig. 2-7), the heavier liquid forms the lower layer and the lighter liquid forms the upper layer. On opening the tap, the lower layer comes down first, followed by the upper layer. Mixture of *benzene and water* can also be separated by this method.

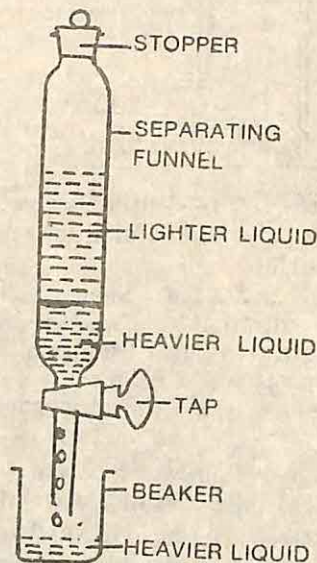


Fig. 2-7. Separation of immiscible liquids by separating funnel

2-4 SEPARATION OF SOME SPECIFIC MIXTURES.

(i) **Mixture of common salt, sand and sulphur.** This mixture is treated with water. Common salt dissolves in water and is separated by filtration. The residue contains sand and sulphur. This mixture of sand and sulphur is treated with CS_2 . Sulphur dissolves in it but sand remains undissolved. On filtration sand is obtained as a residue and sulphur in the filtrate. On evaporation, sulphur is obtained from the filtrate. The filtrate obtained earlier contains common salt. This is evaporated in a china dish. Common salt is left behind in china dish.

(ii) **Mixture containing sand, naphthalene and common salt.** Naphthalene being

volatile is separated by sublimation. Mixture of sand and common salt is treated with water. Common salt dissolves in water and is separated by filtration. Sand remains insoluble. Common salt is recovered from the filtrate on evaporation.

(iii) Mixture containing kerosene oil, water and potassium nitrate. Potassium nitrate is soluble in water. Kerosene oil and water are two immiscible liquids. Kerosene oil being lighter than water forms upper layer. It is separated from water layer using a separating funnel. The water layer contains potassium nitrate dissolved in it. On heating water evaporates and passes to the atmosphere. The residue (potassium nitrate) can be collected.

2-5 PURIFICATION OF SUBSTANCES

The components obtained by separation methods discussed in Section 2-3 are likely to contain other components (as impurities) in small quantities. The component can be purified by repeating the method of separation. The principles of both separation and purification methods are the same. Fractional distillation method is used to obtain pure liquid in case the boiling points of two liquids do not differ much. This technique will be discussed in detail in higher classes. If the liquid impurity has a boiling point nearly 40°C apart than that of the liquid to be purified, a simple distillation technique can be used.

Test of purity. The purity of a substance can be ascertained by determining its melting or boiling point. For a substance to be pure it must give that value of melting point or boiling point which is known to exist for pure substance. With impurities present, the value will vary from the standard value. Crystals also have definite shapes.

Melting point. Melting point of a substance is defined as the temperature at which the solid changes into liquid. A pure substance has a sharp melting point. The apparatus used for the determination of the melting point is shown in Fig. 2-8. Finely powdered substance is taken in a small boiling tube or capillary tube. This is tied to a thermometer with a thread. The bulb of the thermometer is dipped into water taken in a beaker. Heat the water slowly to keep the temperature of water uniform throughout. When the opaque solid becomes transparent the temperature is noted. This is the melting point of the substance. This method is used to determine the melting point of substances which melt below 100°C . For determining the melting point of wax, a small boiling tube is used.

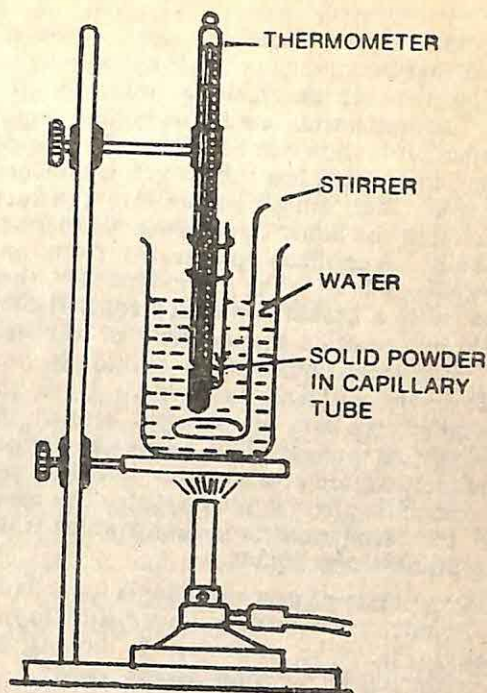


Fig. 2-8. Determination of melting point

Boiling point. The boiling point of a liquid is defined as the temperature at which liquid

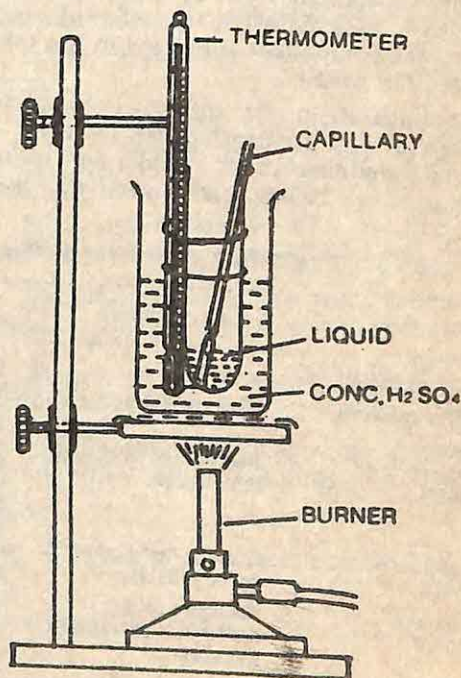


Fig. 2-9 Determination of boiling point

changes into vapour phase. It must, however, be noted that the boiling point is not as reliable test of purity as is the melting point for the solid. The apparatus used for boiling point determination is shown in Fig. 2-9. The liquid is taken in a small test tube which is attached to a thermometer, using a rubber band, in such a way so that the liquid stands near the thermometer bulb. A capillary tube sealed from one end is put into it. The thermometer is then lowered into a beaker containing conc. H_2SO_4 and held in a position keeping half of the test tube above the liquid. The liquid is now heated slowly. When the bubbles leave the lower end of capillary in a rapid stream the temperature is noted. The heating is stopped and the temperature at which the bubbles stop at the end of capillary is also noted. The mean of the two temperatures is found which is the boiling point of the liquid.

Boiling points of organic liquids (or inflammable liquids) are determined by distillation of the liquid (Fig. 2-6). For liquids boiling at higher than 100°C , air condenser is used

2-6 SOLUTION, SUSPENSION AND COLLOIDS

Solutions are homogeneous mixtures of two or more substances. The substance present in the larger concentration is referred as the *solvent*; the component dispersed in the solvent is called the *solute*.

To understand the difference between a solution and a suspension let us take two beakers containing water. Add a tea spoonful of sugar in one beaker and sand in the second

beaker. Shake them well and now allow these beakers to stand undisturbed for about 10 minutes. In the first beaker a homogeneous solution, called true solution results. In this solution, the components do not separate on standing and individual particles of the solute and the solvent cannot be seen, even with the best optical devices. The particle size in a true solution is less than 10^{-7} cm. Here water is solvent and sugar is solute. In the second beaker a heterogeneous solution results, components of which separate upon standing. Here you would observe that some sand particles remain suspended in water making the solution turbid. This turbid solution is called suspension. In a suspension the particle size is greater than 10^{-5} cm. Clay in water, PbSO_4 in water, smoke in air, paints and muddy water are examples of suspension.

Colloids or colloidal solutions appear to be homogeneous mixtures but in true sense these are heterogeneous mixtures. Their particle size is between 10^{-7} and 10^{-5} cm. The solute particles remain suspended in the solvent phase. These particles in suspension constitute the *dispersed phase*; the solvent phase is called the *dispersion medium*. The particles of the dispersed phase are so small that no settling occurs, yet large enough to make the mixture appear cloudy (translucent). Glue in water, starch in water, soap solution, ink, blood, milk, tooth paste, etc. are examples of colloidal systems. In case of glue in water, glue is dispersed phase and water is dispersion medium. Table 2-1 lists the points of difference between three types of solutions.

Table 2-2 Comparative properties of the three solutions - true solution, colloidal solution and suspension

Properties	True solution	Colloidal solution	Suspension
Size of particle	$<10^{-7}$ cm	Between 10^{-7} - 10^{-5} cm	$>10^{-5}$ cm
Type of mixture	Homogeneous	Heterogeneous but appears to be homogeneous	Heterogeneous
Appearance of particles	Invisible even through microscope	Invisible through microscope. Their scattering effect has been characterized through ultra microscope.	Visible to naked eye
Separation of particles	Cannot be separated by any means	Can only be separated by ultra centrifugation	Can be separated by ordinary filtration
Diffusion of particles	Diffuse rapidly through a parchment membrane	Diffuse slowly through a parchment membrane	Cannot diffuse
Tyndall effect	No	Yes	Yes
Brownian movement	No	Yes	Yes

2-7 PROPERTIES OF COLLOIDS

The Tyndall effect : The Tyndall effect is a very interesting phenomenon exhibited by colloidal particles. When a beam of light is passed through a colloidal solution kept in a beaker in a dark room, the path of the light beam is illuminated and becomes visible when

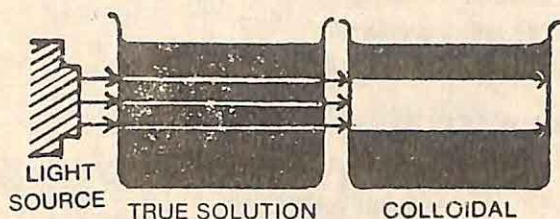


Fig. 2-10. The Tyndall effect : The path of a beam of light can hardly be seen passing through a true solution (left) but is clearly visible in the colloidal dispersion at the right.

seen from the side. This effect is similar to that observed when a beam of sunlight enters a dark room, the dust particles suspended in air are seen in a beam of light. This effect is due to the scattering of light by particles present in the colloidal solution and air. This is called *Tyndall effect*. This is not exhibited by a true solution. The Tyndall effect can be used to differentiate between a colloidal and a true solution (Fig. 2-10).

Brownian movement : Colloidal particles in suspension appear constantly in a state of irregular, rapid and dancing motion. This

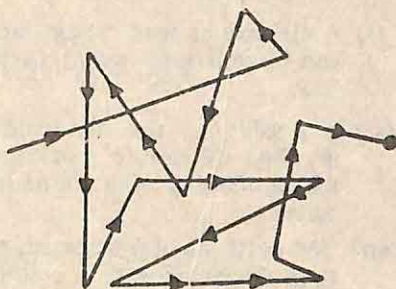


Fig. 2-11 Colloidal particle exhibiting the Brownian movement

erratic motion is called 'Brownian movement' after the name of botanist Robert Brown. In 1828, Robert Brown observed under an ultra-microscope the pollen grains, dispersed in water, moving about in a zig-zag fashion (Fig. 2-11).

The following experiments can be performed in the laboratory.

Experiment 2.1 : To separate components of mixtures of two substances one of which is soluble in water :

Hint : A mixture of salt and sand is a two component mixture. Salt is soluble in water. On filtration, sand could be collected on the filter paper and filtrate could be collected in a beaker. The filtrate is kept in a porcelain dish to evaporate slowly. Crystals of salt start forming after some time. These crystals are separated and purified by crystallization.

Experiment 2.2 : To purify a sample of water by distillation :

Hint : A water sample is generally purified by distillation. The sample is heated and it would boil under atmospheric pressure at a definite temperature (boiling point). Vapours are passed through a water condenser where they get cooled and converted into liquid. The water sample is collected in a receiver.

Other liquids can also be purified by this method.

Experiment 2.3 : To test the purity of a solid by finding its melting point : say naphthalene.

Hint : For details refer to Section 2-5, i.e. Purification of substances—melting point.

Experiment 2.4 : To test the purity of a liquid by finding its boiling point : say alcohol.

Hint : For details refer to Section 2-5, i.e. Purification of substances—boiling point.

Boiling point of alcohol is determined by distillation method (Fig. 2-6)

KEY TERMS

- 2-1 **Substance.** Any variety of matter of recognizably definite composition and specific properties.
- 2-2 **Compound.** A pure substance composed of elements and chemically combined in fixed proportions.
- 2-3 **Mixture.** The product obtained when two or more substances, that do not combine chemically, are mixed in any ratio.

- 2-4 **Heterogeneous mixture.** A mixture with many phases, usually separable by mechanical means.
- 2-5 **Homogeneous mixture.** A uniform mixture having the same specific properties throughout the bulk.
- 2-6 **Colloid.** A heterogeneous mixture in which solute particles do not settle down on dispersing into a solvent phase.
- 2-7 **Dispersed phase.** The solute particles in a colloid.
- 2-8 **Dispersing medium.** The solvent phase in a colloid.
- 2-9 **Tyndall effect.** The scattering of light by colloidal particles.

UNIT THROUGH EXERCISES

2-1 Which of the following substances are mixtures or compounds?

- (i) Gun powder, (ii) Water, (iii) Sea-water, (iv) Vinegar, (v) Ammonia, (vi) Alcohol, (vii) Smoke, (viii) Carbonated water, (ix) Ink, (x) Blood, (xi) Urine, (xii) Soap, (xiii) Glucose, (xiv) Mango juice, and (xv) Alloys.

Ans. (i), (iii), (iv), (vii), (viii), (ix), (x), (xi) (xii), (xiv) and (xv) are mixtures.

2-2 What method would you use to separate the constituents of the following mixtures?

- (i) Ammonium chloride and sodium chloride
- (ii) Iron filings and carbon
- (iii) Salt + water
- (iv) Alcohol (b.p. 78°C) + water (b.p. 100°C)
- (v) Two immiscible liquids (benzene + water)
- (vi) Sand + water

Ans. (i) Sublimation method
(ii) Magnetic method
(iii) Distillation method
(iv) Fractional distillation
(v) Separating funnel method
(vi) Sedimentation method

2-3 Name the term related to the following statements:

- (i) Size of particle is between 10^{-7} – 10^{-5} cm.
- (ii) Colloidal particles appear constantly in a state of irregular rapid and dancing motion.
- (iii) When a beam of sunlight enters a darkened room, scattering of light by the dust particles in the air is observed.

(iv) Particles diffuse rapidly through a parchment membrane.

(v) Particles are visible.

Ans. (i) Colloidal solution, (ii) Brownian motion, (iii) Tyndall effect, (iv) True solution, (v) Suspension

2-4 Choose the true statements of the following:

- (i) Solutions are homogeneous mixtures of only two substances.
- (ii) The Tyndall effect can be used to differentiate between a colloidal and a true solution.
- (iii) On heating, a pure substance melts over a range of temperature.
- (iv) Two miscible liquids are separated using a separating funnel.
- (v) A mixture of iron filings and sulphur can be separated using carbon disulphide.
- (vi) In a solution, the dissolved substance is called the solute and the substance which dissolves the solute is called the solvent.
- (vii) The particles of a suspension are bigger than the particles of a colloid.
- (viii) When two liquids, A (b.p. 110°C) and B (b.p. 80°C) are distilled, liquid B would be distilled first.
- (ix) Glue in water and starch in water represent colloidal systems.
- (x) A mixture of wood and sand can be separated by magnetic method.
- Ans. (i), (ii), (v), (vi), (vii), (viii), and (ix) are true statements.

Multiple Choice Questions**2-5 Pick up the suitable choice :**

1. A mixture of water and ethyl alcohol is known as (homogeneous, heterogeneous).
2. A mixture of chloroform and benzene can be separated by (distillation, sublimation or filtration).
3. On sublimation of a mixture of sand, sulphur, iodine and common salt, the sublimate will be (sand, sulphur, iodine, common salt).
4. A mixture of sugar, sand and sodium chloride is dissolved in water and then filtered through a filter paper. The residue will be (sugar, sand, sodium chloride).
5. Conversion of a solid directly into vapours is called (distillation, sublimation, evaporation).
6. Tyndall effect is shown by a liquid, it must be a (true solution, colloidal solution, pure liquid).
7. The melting point of a substance varies over a range of temperature. The substance is (pure, impure).

- Ans.** 1. homogeneous, 2. distillation,
3. iodine, 4. sand, 5. sublimation,
6. colloidal solution, 7. impure

2-6 Fill in the blanks :

1. Milk is a solution.
2. A mixture of benzene and water can be separated by a process called
3. The mixture does not have a composition.
4. A compound cannot be separated into its constituent elements by means.
5. Smoke is a mixture of and
6. The purity of a substance can be tested by determining its
7. Distillation is a method of purifying

- Ans.** 1. colloidal, 2. separating funnel method, 3. definite, 4. physical, 5. carbon, air, 6. melting point, 7. impure liquids

2-7 Match the statements in column A with those in column B.**Column A**

1. Clay in water
2. Erratic motion
3. Scattering of light
4. Glue in water
5. Solid $\xrightleftharpoons[\text{Cool}]{\text{Heat}}$ vapours
6. Wood + iron filings
7. Gun powder
8. Two immiscible liquids
9. Sharp melting point
10. Liquid $\xrightleftharpoons[\text{Cool}]{\text{Heat}}$ vapours

Column B

1. Pure substance
2. Suspension
3. Magnet
4. Heterogeneous mixture
5. Tyndall effect
6. Colloidal solution
7. Sublimation
8. Brownian motion
9. Separating funnel
10. Distillation

REVIEW QUESTIONS

- 2-1 Distinguish among solute, solvent and solution.
- 2-2 Distinguish between solution and colloid. Give examples of each.
- 2-3 How would you determine whether an unknown liquid is a colloidal solution or a true solution?
- 2-4 Describe a method to separate the constituents of gun powder.
- 2-5 Describe briefly how would you separate benzene (b.p. 80°C) and aniline (b.p. 184°C).
- 2-6 Give the differences between evaporation and sublimation.
- 2-7 Give reasons to show that air is a mixture of gases and water is a compound.
- 2-8 How will you separate the mixture comprising the following constituents?
- (a) Iron powder and carbon
 - (b) Common salt, iodine and sand
 - (c) Sugar and sulphur
 - (d) Iron filings, common salt, sand and sulphur
- 2-9 What is the Tyndall effect and how is it caused?
- 2-10 Put $\checkmark$ or $\times$ in the squares:
- (i) Brass is an example of a compound. ☐
 - (ii) Glass is an example of a heterogeneous mixture. ☐
 - (iii) Benzene is a solid organic compound. ☐
 - (iv) Milk is a homogeneous mixture. ☐
 - (v) Mercury is a liquid non-metal. ☐

☐

UNIT 3

Structure of Atom and Chemical Bonding



Ernest Rutherford
(1871—1937)

Rutherford is best known for his theories of radioactive decay and of the structure of atom. He discovered the three kinds of rays emitted by radioactive substances. He discovered atomic nucleus and developed the nuclear model of the atom, thus laid the foundation of the modern science of the structure of the atom. In 1908, he was awarded the Nobel Prize.

Learning Objectives :

At the completion of this unit, you should be able to :

1. Give the postulates of the Dalton's atomic theory.
2. Comment on the cathode rays.
3. Prove the existence of protons.
4. Account for the mass of an atom through the existence of neutron.
5. Explain the observations made with Rutherford's experiment.
6. Explain why the Rutherford's atomic model is not satisfactory.
7. Describe the Bohr's model of the atom.
8. Explain the term atomic number.
9. State the relationship between the nuclear structure and the atomic and mass numbers.
10. Calculate the maximum number of electrons that can occupy each principal energy level in an atom.
11. Write the electronic configuration of an atom.
12. State what is meant by an isotope.
13. Define and state the usefulness of valence electrons.
14. Define the chemical bond.
15. Write electron dot formulae for atoms and chemically combined atoms.

16. Understand the significance of 'octet rule'.
17. State what is meant by ions.
18. Recognize that, as a general rule, elements tend to combine to form compounds in which they have a noble gas structure.
19. Explain how, ionic and covalent bonds are formed between atoms.
20. State the conditions governing the formation of ionic and covalent bonds.
21. Explain the formation of a dative or coordinate bond.
22. Describe the formation of multiple bonding in simple molecules.
23. Differentiate between covalent and ionic compounds.
24. Write Lewis structures for the various molecules.
25. Understand the origin of polarity in covalent molecules and thus distinguish between polar molecules and polar bonds.

3-1 INTRODUCTION

According to the ancient Greeks, in particular the philosopher Democritus, all the materials and objects present in the universe are composed of the smallest indivisible and indestructible particles. These particles were thought to be in constant motion but able to fit together into stable combinations. Today, these particles are referred to as atoms.

On the basis of the simple notions of the Greeks and certain quantitative data (laws of chemistry) available, John Dalton put forward his famous atomic theory (Unit 1).

Today, of course, our model of the atom is vastly more sophisticated than Dalton's. The atom is more complex than his solid-sphere concept, which he developed without knowledge of the subatomic particles called, electrons, protons and neutrons. The observations that led to a gradual refinement and extension of the atomic theory are numerous indeed, a detailed description of all of them is beyond the purpose of this book. However, a brief account of some of the more significant break-throughs is given here.

As we know, compounds are substances formed by the combination of atoms of two or more elements. The properties of compounds and the nature of the bonding between their constituent atoms will also be discussed in this unit.

THE STRUCTURE OF THE ATOM

3-2 CATHODE RAYS (ELECTRONS)

One of the first significant advances, after the Dalton's atom, was made by J.J. Thomson (1898) and Lenard. They passed electric discharges through gases. This led to the

discovery of negatively charged particles. Basically, their device consists of a closed glass tube, into the ends of which are sealed two metal plates to serve as electrodes. A high voltage (5000-10,000 volts) is imposed across the electrodes (Fig. 3-1). If the air (or other gas say neon, mercury vapour, helium, etc.) in the tube is at atmospheric pressure, nothing is observed.

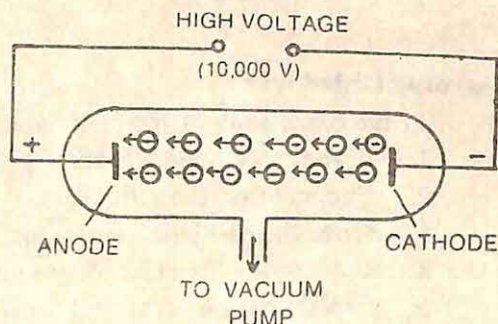


Fig. 3-1. Formation of cathode rays. Electrons are flowing from cathode to anode in a gas discharge tube.

However, if most of the air is pumped out of the tube, the remaining air begins to glow and conducts the electric current. On lowering the pressure, the appearance of the tube changes. At sufficiently low pressures, the glow fades, although current continues to flow and the end of the glass tube with anode (the positive electrode) fluoresces (emits light). The fluorescence at the anode of the tube is caused by the rays emerging from the cathode and moving towards the anode. These rays are called *cathode rays* because they originate at the cathode.

Thomson performed a series of experiments that permitted him to illustrate the important features of cathode rays; their results are noted below:

1. **The cathode rays travel in straight lines.** When a metallic object is placed in the path of the cathode rays, a shadow is cast upon the wall opposite the cathode (Fig. 3-2).

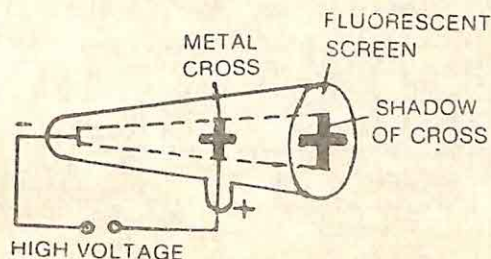


Fig. 3-2. Cathode rays travel in straight lines and cast shadow of the object placed in their path upon the wall opposite the cathode.

Also, if a metal plate (Fig. 3-3) with a hole (anode) in it is placed in front of the cathode and the end opposite the cathode is coated with a fluorescent substance, a bright spot of light can be seen.

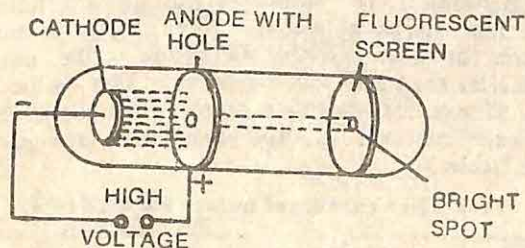


Fig. 3-3. Movement of cathode rays. They move in straight lines and originate at the cathode.

The shadow of the metal object on the wall opposite the cathode and the size of the spot on the fluorescent screen compared to the size of the hole in the anode shows that cathode rays travel in straight lines.

2. **The cathode rays consist of particles.** If a paddle wheel is placed in the path of the rays, it starts rotating (Fig. 3-4). This movement establishes that cathode rays consist of particles which can impart their momentum to the wheel.

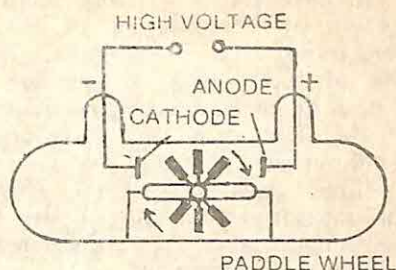


Fig. 3-4. Cathode rays impart mechanical motion to a paddle wheel placed in their path. They possess kinetic energy.

3. **The cathode rays consist of negatively charged particles.** A magnet placed outside the tube causes the spot of light to move at right angles to the direction of the magnetic field (Fig. 3-5). The direction of the deflection suggests that the cathode rays carry a negative electric charge. The cathode rays, when pass through a strong electric field experience deflection (Fig. 3-6). They move towards the positively charged electrode. This also shows that the rays carry a negative charge.

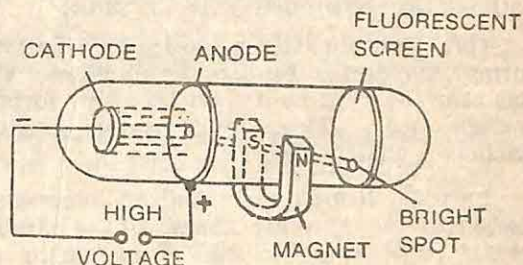


Fig. 3-5. Effect of a magnetic field on cathode rays. They are deflected by a magnetic field. The downward deflection shows that the cathode rays are negatively charged.

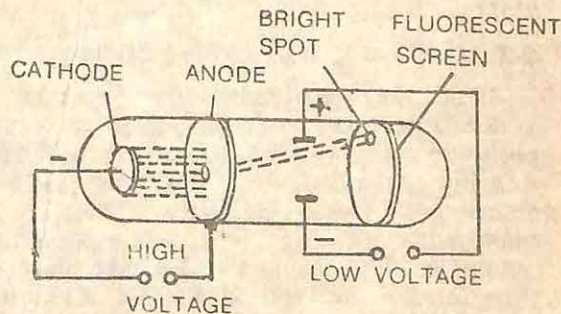


Fig. 3-6. Effect of an electric field on cathode rays. They are deflected by an electric field.

4. The cathode rays have same e/m irrespective of the nature of electrode and gases used. J.J. Thomson studied the behaviour of these rays by passing them through both magnetic and electric fields. He adjusted the fields such that the cathode rays strike the fluorescent screen at the same spot as when neither field is present (Fig. 3-7). Thomson measured the ratio of the electric charge 'e' to mass 'm' of the particles in cathode rays by using this experiment.

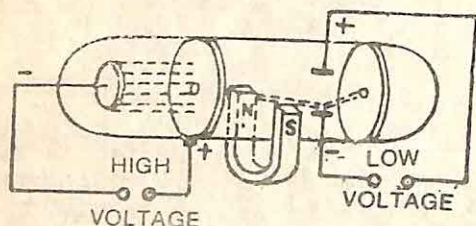


Fig. 3-7. An assembly for measurement of e/m for the particles constituting cathode rays

Thomson performed a series of experiments by using different metal of electrodes and different gases in the tube. In all the arrangements, the charge to mass ratio, e/m , for cathode rays was found to be the same.

This establishes that such negative particles form a common constituent of all gases. This has been found to hold good for other form of matter also. This fundamental negative particle is named *electron*.

In 1907, Robert A. Millikan successfully measured the absolute charge of the electron (4.80×10^{-10} esu or 1.6×10^{-19} coulomb) and made it possible to calculate its mass. The electron's mass was determined to be 9.11×10^{-28} g (0.000548 amu) which approximates $\frac{1}{1840}$ of the mass of the hydrogen atom.

3.3 POSITIVE RAYS (PROTONS)

If electrons are observed near the anode in a discharge tube, isn't it logical to expect positively charged particles near the cathode? Actually, a radiation of this type has been observed by Eugen Goldstein (1886). He employed a discharge tube with a perforated cathode as illustrated in Fig. 3-8, and observed glow (at low pressure) at the end of the tube beyond the cathode. This glow was caused by the rays emanating through the perforated cathode. These rays were called *canal rays*

by Goldstein, since they moved towards cathode and finally passed through the holes (or canals) in the cathode. Unlike the cathode rays (which are not apparent unless they strike an object that fluoresces, such as glass), canal rays possess a luminosity of their own. Furthermore, the colour of the luminosity changes with the gas contained in the tube.

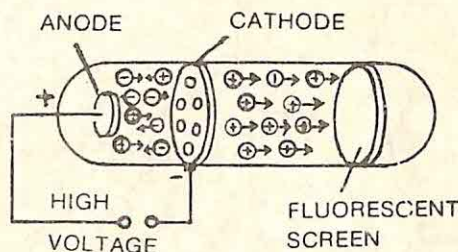


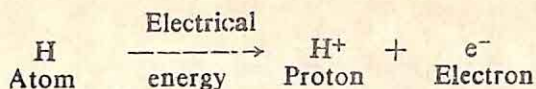
Fig. 3-8. Formation of canal rays

Wilhelm Wien investigated Goldstein's observations thoroughly and showed that canal rays are consisted of particles which are deflected towards the negative pole in an electric field and must therefore be positively charged. Wien determined the charge to mass ratio of these particles using a technique similar to Thomson's employed in the studies of electrons. He obtained different results depending on the nature of the gas contained in the discharge tube. The charge to mass ratio for these particles was found to be much smaller than e/m for electrons. The value is maximum for hydrogen atom. The characteristics of cathode rays and canal rays are given in Table 3-1.

Table 3-1 Properties of cathode and canal rays

S. No.	Cathode rays	Canal rays
1.	Composed of negatively charged particles, called electrons	Composed of positively charged ions
2.	Move in straight lines	Move in straight lines
3.	Possess kinetic energy and momentum	Possess kinetic energy and momentum
4.	e/m of their particles is always the same	e/m of their particles depends upon the nature of gas

When an electron is removed from hydrogen atom, the positive particle left behind is called a proton (from the Greek word 'protos' meaning first)



The proton is a fundamental particle and a constituent of all atoms whose charge is equal to that of the electron, but opposite in sign. The mass of a proton is equal to the mass of a hydrogen ion, i.e., 1.67×10^{-24} g (1.007 amu).

3-4 THOMSON'S MODEL OF ATOM

The discovery of electron and proton provided evidence against the indivisibility of the atom. These particles provided scientists with a simple model of atomic structure. A hydrogen atom could now be considered to consist of two parts a positively charged proton, accounting for all the mass of atom, and a negatively charged, extremely light electron.

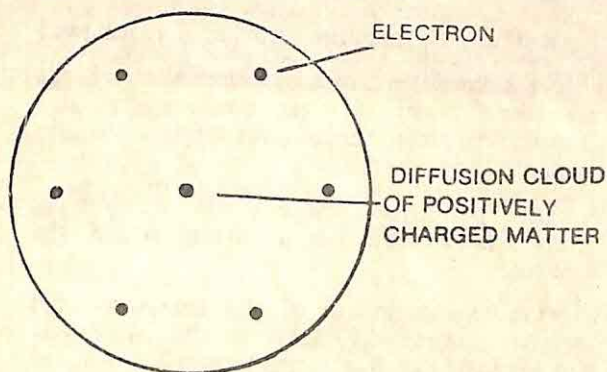


Fig. 3-9 Thomson's model of the atom.

Around the turn of the century, several attempts were made to extend this model of the hydrogen atom to a general one that would apply to all atoms. One such model was created by Thomson in 1904. He regarded the atom as consisting of a diffuse cloud of positively charged body (positive charge is uniformly spread throughout the spherical volume of the atom) in which negatively charged electrons are embedded throughout (Fig. 3-9). This has been referred to as the '*plum pudding model*' by Thomson. His model could explain the phenomena of cathode ray production, light emission and ionization. However, no quantitative explanation could be achieved of these phenomena.

3-5 RUTHERFORD'S EXPERIMENT (The scattering of α -particles)

Sir Ernest Rutherford (1911) directed a narrow beam of α -particles (positively charged helium ion) from a radioactive material towards an extremely thin strip of gold (Fig. 3-10) and determined the subsequent path of the particles (Fig. 3-11).

A fluorescent screen was set up around the foil. He made the following observations :

(i) Most of the α -particles passed straight through the metal foil to hit the fluorescent screen ;

(ii) Some α -particles were deflected through a small angle from their original paths ;

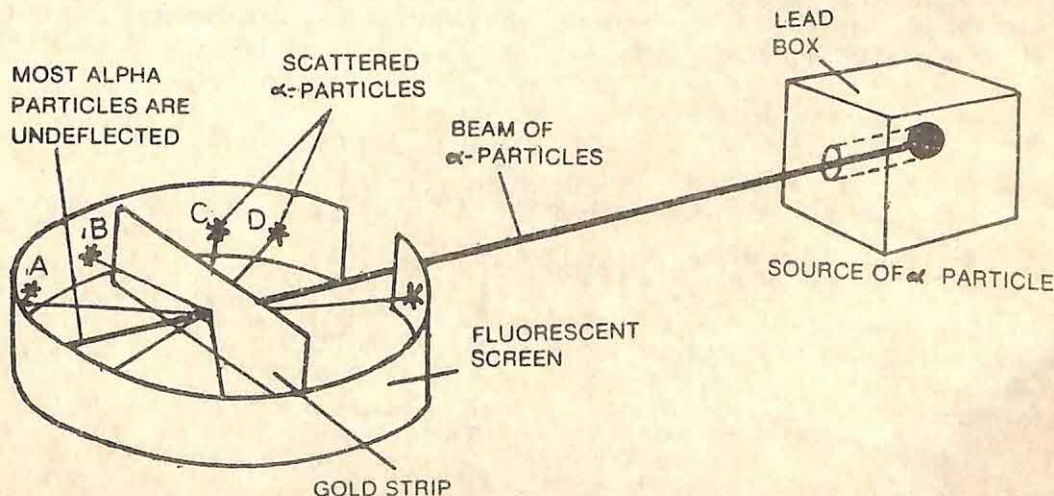


Fig. 3-10. Rutherford's α -particles scattering experiment

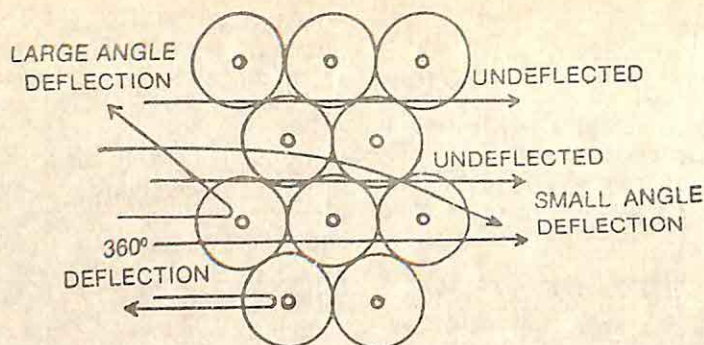


Fig. 3-11 The general pattern of scattering of α -particles by a gold strip made up of atoms

(iii) A few α -particles were deflected through very large angles ; and

(iv) Very few α -particles actually bounced back in the direction from which they came.

Rutherford reasoned as follows :

Since most of the α -particles pass through the gold strip without experiencing deflection, there seems to be a lot of empty space within an atom.

The angles through which the individual α -particles are deflected vary widely. Deflections reveal the following :

(i) The α -particles are deflected due to collision with the central part of the atom.

(ii) The central part of the atom is positively charged, hence, the positively charged α -particles are repelled by it.

(iii) The fact, that very few α -particles are deflected through large angles, shows that the positive charge is contained in a very small space. However, because the kinetic energy of

an α -particle is very large, only a massive particle with high charge within the metal atom could cause deflection through such large angles.

Rutherford, therefore, concluded as follows :

(i) Mass of an atom and its positive charge are concentrated in a very small region called the *nucleus*—the atom is mostly 'empty space'.

(ii) The nuclear charge is balanced by negatively charged electrons revolving round the nucleus.

(iii) The magnitude of the charge on the massive nucleus is different for different atoms and is nearly one half of the numerical value of the atomic weight.

Rutherford, thus, described that each atom consists of nucleus (positively charged) around which electrons (negatively charged) are revolving (Fig. 3-12 a). In the atom of an element

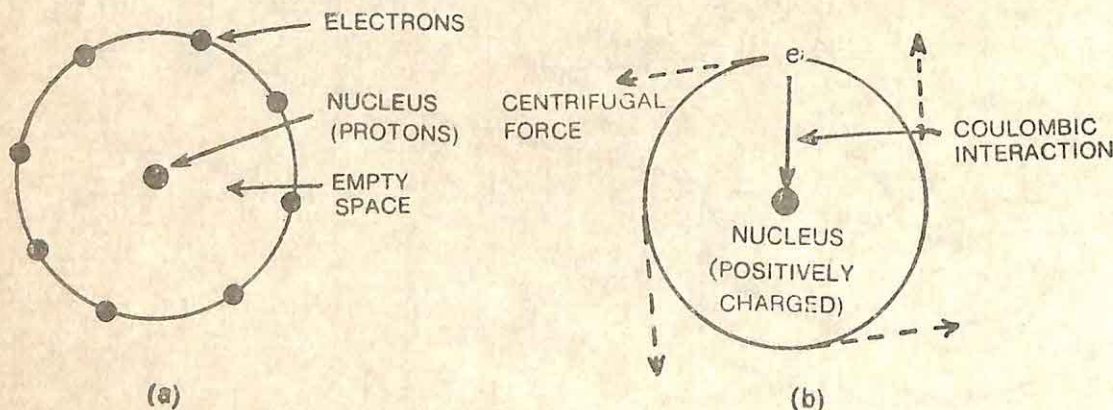


Fig. 3-12: Rutherford's planetary model of the atom

the number of electrons is the same as the number of protons in its nucleus. Further to account for the stability of the atom, he suggested that the electrons revolve round the nucleus with high velocities. The centrifugal force so produced counterbalances the coulombic force of attraction between the oppositely charged particles (Fig. 3-12 b).

This was a beautiful model. Its logical simplicity was impressive, since it seemed to be like our solar system (planets move around the sun). However, the planets and the sun are not electrically charged particles.

3-6 THE NEUTRON

Rutherford (1920) had suggested that in addition to the two charged particles in an atom, there was the possibility of the presence of a particle of essentially the same mass as that of a proton but without any charge.

James Chadwick (1932) showed the existence of neutrons (neutral particles) as well as protons in the nucleus of atoms by bombarding boron, beryllium or lithium metal with α -particles (Fig. 3-13). He observed that the radiations emitting from the metal did not experience

any deflection in the magnetic field, hence, Chadwick noted that these radiations must consist of particles that did not possess any electrical charge. On allowing these radiations to strike a block of paraffin placed in their path, protons were ejected from the paraffin. The particles in this new form of radiations were able to collide with hydrogen atoms (paraffin contains hydrogen atoms) and cause their ejection by direct collision. Chadwick observed that only a particle similar in mass to the proton could be able to collide with hydrogen atoms. He called these particles, the *neutrons*. Table 3-2 lists the basic physical properties of the atomic particles.

3-7 BOHR'S CONCEPT OF ATOM

Rutherford's atomic model provides a reasonable view of the atom but it does not convey regarding the positions of electrons relative to each other and to the nucleus or to their state of motion around the positively charged nucleus.

To circumvent the objections levelled against the Rutherford's atomic model, Niels Bohr in 1913 put forward his theory regarding the structure of atom. He retained the main

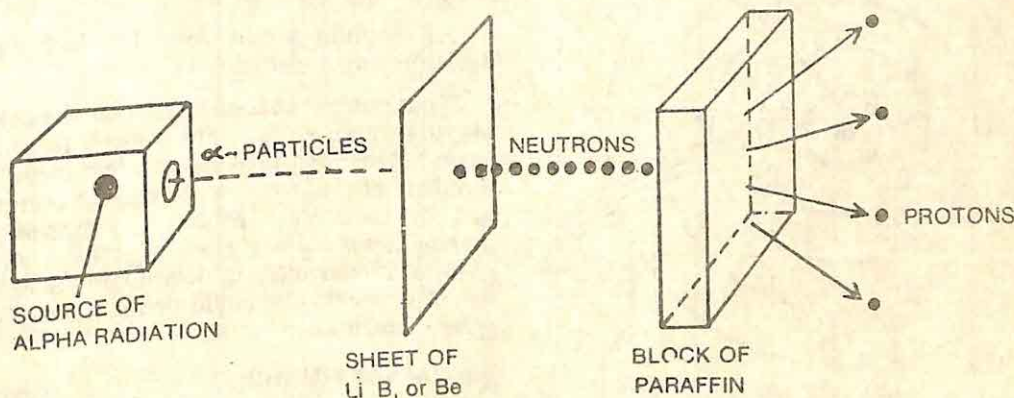


Fig. 3-13 An assembly to produce neutrons

Table 3-2 Properties of atomic particles

Particle	Symbol	Mass	Charge	Location
Electron	e	1/1840 of a hydrogen atom	Negative charge, 1.6×10^{-19} coulomb (1 unit)	Revolves round the nucleus
Proton	p	Equal to that of a hydrogen atom	Positive charge ; equal and opposite to that of electron (1 unit)	Present in the nucleus
Neutron	n	Equal to that of a hydrogen atom	No charge	Present in the nucleus

features of the nuclear model of the atom suggested by Rutherford and proposed some modifications. The proposed model is known as Bohr's model.

The salient features of Bohr's model of the atom are :

1. The nucleus of an atom is situated at its centre.
2. The electrons in an atom move around the nucleus in definite circular orbits known as energy levels (or shells).
3. Each energy level is associated with a fixed amount of energy. These energy levels are also called allowed or stationary states because the energy of the electrons remains constant as long as they keep on moving in the same energy level.
4. These energy levels starting from the one close to nucleus, are numbered as 1, 2, 3, 4, etc. or designated as K, L, M, N, etc. (Fig. 3-14).

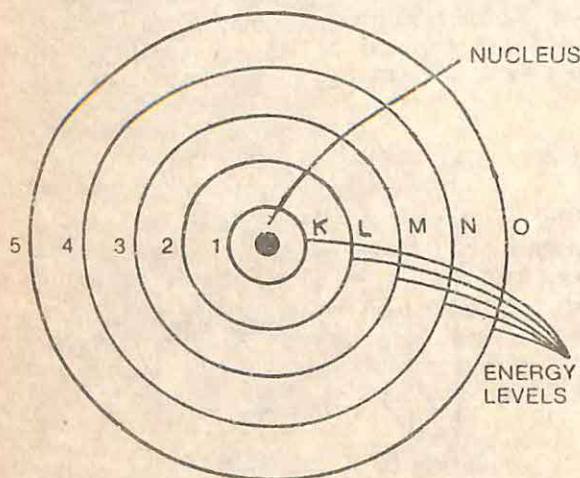


Fig. 3-14. Bohr's model of an atom

5. An electron neither loses nor gains energy if it keeps moving in one of these stationary states.

6. An electron can move only from one energy level to another. In such transitions, it either absorbs or emits a fixed amount of energy, i.e., the change in the energy of an electron takes place.

7. When an electron jumps from a higher energy level to a lower energy level it emits energy; when it jumps from a lower level to a higher energy level it absorbs energy.

3-8 ATOMIC NUMBER

Rutherford's work established that the mass of an atom and the mass of its nucleus are essentially equal since the mass of electrons is very small. He could not assign a precise positive charge to the nucleus. The magnitude of this charge was found by Henry G. J. Moseley (1913) in experiments with X-ray spectra. From Moseley's relation, it was found that the number of unit positive charges on the nucleus is known as the *atomic number* of the element. It is denoted by Z . All atoms of a particular element have the same nuclear charge. Moseley investigated the positive charge on the nucleus of atoms of different elements. Since an atom is electrically neutral, the atomic number is also equal to the total number of electrons in the orbits (shells) of an atom of the element. Thus,

$$\text{Atomic number, } Z = p = e$$

Moseley's work, thus, allows us to state that :

All hydrogen atoms have 1 electron and nuclei having a charge of +1.

All oxygen atoms have 8 electrons and nuclei having a charge +8.

All sodium atoms have 11 electrons and nuclei having a charge +11.

Thus nuclear charge determines the chemical identity of an atom. The element to which an atom belongs is, therefore, determined by its number of electrons or its nuclear charge, and not by its mass. Moseley suggested that *atomic number was more significant than the relative atomic mass* in determining the properties of elements and could be the basis of classifying elements.

3-9 MASS NUMBER

The total number of protons and neutrons contained in the nucleus of an element is called its *mass number*. It is denoted by A . The mass number is always a whole integer. Thus,

$$\begin{aligned} \text{Mass number, } A &= n + p \\ &= n + Z \end{aligned}$$

Protons and neutrons are collectively known as *nucleons*. These particles are extremely tightly packed together in the nucleus. The difference of mass number and atomic number equals the neutron number. Thus,

$$A - Z = \text{Number of neutrons}$$

For a hydrogen atom, the mass number is equal to its atomic number because there is no neutron in a hydrogen atom. A helium atom contains 2 protons and 2 neutrons. Therefore, the mass number of helium atom is 4. A particular atom with an atomic number of 17 and a

mass number of 35, therefore, contains 17 protons and 18 neutrons in its nucleus and has 17 extranuclear electrons. Table 3-3 illustrates the number of protons, neutrons and electrons and atomic and mass numbers for the atoms of some common elements.

Table 3-3 Atomic number and mass number of some common elements

Element	Notation	Atomic number (Z)	Mass number (A)	Number of protons (Z)	Number of neutrons (A-Z)	Number of electrons
Hydrogen	${}^1_1\text{H}$	1	1	1	0	1
Helium	${}^4_2\text{He}$	2	4	2	2	2
Lithium	${}^7_3\text{Li}$	3	7	3	4	3
Beryllium	${}^9_4\text{Be}$	4	9	4	5	4
Boron	${}^{11}_5\text{B}$	5	11	5	6	5
Carbon	${}^{12}_6\text{C}$	6	12	6	6	6
Nitrogen	${}^{14}_7\text{N}$	7	14	7	7	7
Oxygen	${}^{16}_8\text{O}$	8	16	8	8	8
Fluorine	${}^{19}_9\text{F}$	9	19	9	10	9
Neon	${}^{20}_{10}\text{Ne}$	10	20	10	10	10
Sodium	${}^{23}_{11}\text{Na}$	11	23	11	12	11
Magnesium	${}^{24}_{12}\text{Mg}$	12	24	12	12	12
Aluminium	${}^{27}_{13}\text{Al}$	13	27	13	14	13
Silicon	${}^{28}_{14}\text{Si}$	14	28	14	14	14
Phosphorus	${}^{31}_{15}\text{P}$	15	31	15	16	15
Sulphur	${}^{32}_{16}\text{S}$	16	32	16	16	16
Chlorine	${}^{35}_{17}\text{Cl}$	17	35	17	18	17
Argon	${}^{40}_{18}\text{Ar}$	18	40	18	22	18
Potassium	${}^{39}_{19}\text{K}$	19	39	19	20	19
Calcium	${}^{40}_{20}\text{Ca}$	20	40	20	20	20

To designate a specific atom and its nuclear contents, the symbol for the element with the atomic number as subscript and the mass number as a superscript, both to the left of the symbol, is written, e.g., ${}^4_2\text{He}$. Table 3-3 also illustrates this notation.

3-10 DISTRIBUTION OF ELECTRONS IN DIFFERENT ENERGY LEVELS (ELECTRONIC CONFIGURATION)

In 1913, Niels Bohr visualized the atom as a miniature solar system with electrons orbiting the nucleus at definite distance from the nucleus in circular shells or energy levels (or orbits). An energy level is a region around the nucleus in which an electron may most probably be found. The first energy level is near the nucleus and has the lowest energy. Relative energy content increases with the distance from the nucleus.

Bohr and Bury suggested a scheme for the distribution of electrons in various shells on the basis of certain experimental facts. The systematic distribution of electrons in various energy states or shells of an atom is called the *electronic configuration*. Accordingly:

1. The electrons are arranged around the nucleus in different energy levels or shells. The distribution of electrons follows the 'aufbau principle'. The aufbau principle says that electrons first occupy the shell with the lowest energy and then move towards the higher energy levels.

2. The maximum number of electrons to be accommodated in any energy level of an atom is given by $2n^2$, where n represents the number of the energy level (n is called the principal quantum number; its values are 1, 2, 3, 4...). These values refer to the energy levels. Thus the maximum number of electrons in the first shell, i.e., K-shell ($n=1$) is 2; in the second shell, i.e., L-shell ($n=2$) is 8; in the third shell, i.e., M-shell ($n=3$) is 18; and so on. Distribution among the various shells is given below:

Energy level n	Name	$2n^2$	Maximum electron population
1	K-shell	$2(1)^2$	2
2	L-shell	$2(2)^2$	8
3	M-shell	$2(3)^2$	18
4	N-shell	$2(4)^2$	32
5	O-shell	$2(5)^2$	50

3. In the outermost shell of any atom, the maximum possible number of electrons is 8 except in the first shell which can have at the most 2 electrons.

4. The penultimate shell (just before the outermost) cannot have more than 18 electrons.

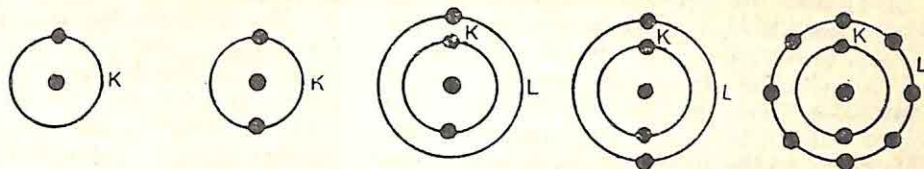
5. It is not essential for a shell to be completed according to the 2nd rule before electrons fill the next shell. When a shell acquires 8 electrons, a new shell with electrons in it may be formed.

To visualize the distribution of electrons in greater detail a pictorial representation of a few atoms is given in (Fig. 3-15).

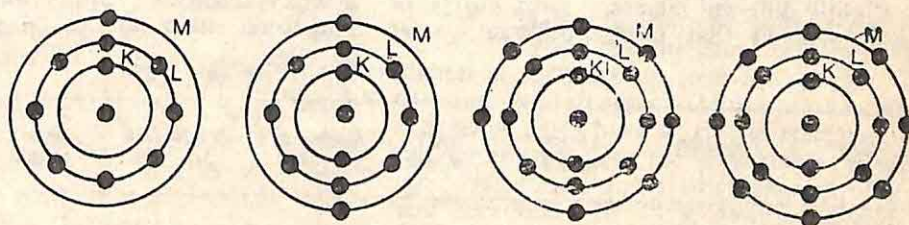
A helium atom contains 2 electrons which occupy the K-shell. A lithium atom contains 3 electrons. Of these 3 electrons, K-shell has 2 electrons to its full capacity according to $2n^2$ rule. The third electron of lithium occupies the L-shell. Now as the atomic number increases the electrons continue to occupy the L-shell till it contains 8 electrons to its full capacity according to $2n^2$ rule. In neon atom, there are 10 electrons. The first two electrons occupy the K-shell and the next 8 electrons occupy the L-shell. Now the next sodium atom has 11 electrons—two electrons occupy the K-shell, 8 electrons occupy the L-shell. The eleventh

Table 3-4. Distribution of electrons for the first twenty elements

Element (symbol)	Atomic number	Distribution of electrons			
		K ($n=1$)	L ($n=2$)	M ($n=3$)	N ($n=4$)
H	1	1			
He	2	2			
Li	3	2	1		
Be	4	2	2		
B	5	2	3		
C	6	2	4		
N	7	2	5		
O	8	2	6		
F	9	2	7		
Ne	10	2	8		
Na	11	2	8	1	
Mg	12	2	8	2	
Al	13	2	8	3	
Si	14	2	8	4	
P	15	2	8	5	
S	16	2	8	6	
Cl	17	2	8	7	
Ar	18	2	8	8	
K	19	2	8	8	1
Ca	20	2	8	8	2



ELEMENT	H	He	Li	Be	Ne
ATOMIC NUMBER	1	2	3	4	10
DISTRIBUTION OF ELECTRONS IN SHELLS	K 1 L	2	2 1	2 2	2 8



ELEMENT	Na	Mg	Cl	A
ATOMIC NUMBER	11	12	17	18
DISTRIBUTION OF ELECTRONS IN SHELLS	K 2 L 8 M 1	2 8 2	2 8 7	2 8 8

Fig. 3-15. Distribution of electrons in various energy levels

electron goes to the *M*-shell. Accordingly, the electronic configuration of the last atom, Argon shown in Fig. 3.15 is 2, 8, 8.

The distribution of electrons for the first twenty elements is given in Table 3-4.

3-11 ISOTOPES

The mass of an atom is mainly attributed to the masses of protons and neutrons contained in its nucleus (the electrons have negligible mass.) Since the relative atomic masses of proton and neutron are virtually equal to one, it would be presumed that all the elements would have their relative atomic masses

very close to whole numbers. But this is true only in a few cases, *e.g.*, helium, oxygen and aluminium. The relative atomic masses of helium, oxygen and aluminium are 4.0026, 15.999 and 26.982 respectively. The relative atomic masses of other elements are far from being near whole numbers, *e.g.*, neon (20.183), magnesium (24.312) and chlorine (35.5). Now the question arises as to why are the relative atomic masses of some of the elements not close to whole numbers? In nineteenth century chemists were able to determine relatively accurate atomic weights for all the elements.

Now take the case of chlorine for which atomic mass is 35.5. One chlorine atom contains 17 protons and 18 neutrons. The atomic mass of chlorine due to 17 protons and 18 neutrons is $(17 \times 1.0 + 18 \times 1.0) 35$. The determined value is 35.5. The explanation of this difference and the answer to the question raised earlier has been given by considering the existence of isotopes. Natural occurring chlorine consists of two isotopes, one represented by $^{35}_{17}\text{Cl}$ (75%), and the other by $^{37}_{17}\text{Cl}$ (25%). The average atomic mass is

$$\left(35 \times \frac{75}{100} \right) + \left(37 \times \frac{25}{100} \right) = 26.25 + 9.25 \\ = 35.5$$

In 1911, F.W. Aston also showed that atoms of some naturally occurring elements have slightly different masses. Thus, atoms of the same element that possess different masses

are called the *isotopes* of the element. Isotope is a Greek word. 'Iso' is for same and 'tope' is for place. Therefore, the isotopes of an element occupy the same place in the periodic table. Isotopes have the same number of protons (or same atomic number) but different number of neutrons (or different mass number) in their nuclei.

As the isotopes of any element have the same number of protons, they should also have the equal number of electrons. Therefore, they show similar chemical properties because these depend upon the electronic configuration of the atom. Neutrons have little influence on the chemical properties of elements. They contribute to the mass of the atom and are responsible for the existence of isotopes.

Isotopes have different physical properties such as densities, melting and boiling points and some other physical properties. This is

Table 3-5. Composition of some common isotopes

Isotopes	Notation	Atomic Number	Mass Number	Number of protons	Number of neutrons	Atomic weight	Number of electrons
(Hydrogen-1 (Protium))	^1_1H	1	1	1	0	1.008	1
Hydrogen-2 (Deuterium)	^2_1H	1	2	1	1	2.014	1
Hydrogen-3 (Tritium)	^3_1H	1	3	1	2	3.022	3
Lithium-6	^6_3Li	3	6	3	3	6.015	3
Lithium-7	^7_3Li	3	7	3	4	7.016	3
Carbon-12	$^{12}_6\text{C}$	6	12	6	6	12.000	6
Carbon-14	$^{14}_6\text{C}$	6	14	6	8	14.003	6
Carbon-13	$^{13}_6\text{C}$	6	13	6	7	13.003	6
Nitrogen-14	$^{14}_7\text{N}$	7	14	7	7	14.003	7
Nitrogen-15	$^{15}_7\text{N}$	7	15	7	8	15.000	7
Oxygen-16	$^{16}_8\text{O}$	8	16	8	8	15.995	8
Oxygen-17	$^{17}_8\text{O}$	8	17	8	9	16.999	8
Oxygen-18	$^{18}_8\text{O}$	8	18	8	10	17.999	8
Chlorine-35	$^{35}_{17}\text{Cl}$	17	35	17	18	34.970	17
Chlorine-37	$^{37}_{17}\text{Cl}$	17	37	17	20	36.970	17

because of the fact that isotopes contain different number of neutrons in their nuclei.

Table 3-5 summarizes the composition of some common isotopes.

3-12 VALENCE ELECTRONS

The electronic configuration of nitrogen is 2, 5, i.e., 2 electrons in *K*-shell and 5 electrons in *L*-shell. The electrons present in *L*-shell, i.e., the outermost shell of the nitrogen atom are called the *valence electrons*. These electrons take part in the chemical combination of atoms. Thus, these electrons also decide the combining capacity of an atom, and hence, *valency*. The shell containing the valence electrons is called *valence shell*. The number of valence electrons present in the nitrogen atom is 5. The valence shell is the *L*-shell.

The number of valence electrons of an element also tells us about the periodic group number of an element. For example, hydrogen, sodium and potassium contain one electron each in their valence shells and all these elements belong to the first group. Some other elements, e.g., both magnesium and calcium contain 2 electrons in their valence shells and hence, claim their position in the second group of the periodic table (Unit 4).

The valency of an element is given either by its number of valence electrons, i.e., the periodic group number (*G*) and/or by (8-*G*). For example, the valency of elements like Na, Mg and Al is 1, 2, 3 respectively, i.e., same as the number of their valence electrons. For some other elements like, nitrogen, oxygen and fluorine the valency is calculated by subtracting the number of valence electrons from 8 (or 8-periodic group number). Thus, nitrogen, oxygen and fluorine have valency, 3, 2 and 1 respectively.

In a group, the number of valence electrons remains the same. In a period, the number of valence electrons increases on going from left to right.

Helium, neon and argon with 2, 8, and 8 electrons respectively in their outermost shells are known as inert elements or noble gases. Their inertness is attributed to the stable electronic arrangement.

CHEMICAL BONDING

3-13 CHEMICAL BONDING

In 1803, Dalton proposed that atoms united with one another in order to form stable

molecules. This assumption proved to be correct, and was a major step in the advancement of chemistry. But it also posed many questions: Why do atoms unite together to form molecules? What keeps the atoms united and how is bonding achieved?

Following the discovery of the electron and the development of theories of atomic structure, it was suggested that the electrons revolving round the nucleus were involved in the formation of chemical bonds between the atoms. It was soon realized that for many elements the number of outermost electrons was related directly to the valency. Thus the alkali metals with one electron in the outermost shell have a monovalency, the alkaline earth metals with two outermost electrons have a bivalency, etc. It is, therefore, customary to speak of the outermost electrons as valence electrons.

The first clue to the chemical combination came only from the structure of noble gases and their remarkable inability to enter into chemical combination. It is fair to assume that noble gases have a stable electronic configuration and that the unreactive nature of these elements is due to their special electronic configuration. In 1916, Walter Kossel and Gilbert N. Lewis independently advanced the view that atoms tend to react together so as to attain the stable electronic configurations of the nearest noble gases. In the process of combining, atoms attain either the stable electronic configuration of helium or the configuration of some other gas. Since the atoms of noble gases, with the exception of helium, have eight electrons in their outermost shell, the Kossel-Lewis theory became known as the '*octet rule*'. There are many exceptions to the octet rule, but it is still a very useful concept for understanding the chemical bond.

When two similar or dissimilar atoms approach each other, both attractive and repulsive forces start acting on them. As a consequence of these forces, the electrons present in the outermost shells of the atoms rearrange themselves to attain the stable structure of the nearest noble gas. As a result of rearrangement, a molecule forms if the forces of attraction are stronger than the forces of repulsion. Thus the attractive force is termed as *chemical bond*. During the formation of a chemical bond, energy is either evolved or absorbed depending on the nature of the reacting substances and the bonds that are formed.

The octet theory states that in a chemical bond formation, atoms tend to gain, lose or share electrons to achieve the stable electronic configuration of a noble gas. Generally this happens through the formation of one or the other type of bond—ionic (or electrovalent) covalent or coordinate.

3-14 THE IONIC (OR ELECTROVALENT) BOND

Ionic bond results from the force of attraction between oppositely charged ions. Ions are formed when electrons are transferred from one atom to another. As a result of transfer of electrons, ions acquire stable electronic configuration similar to those of the nearest noble gas. Let us consider this process in more detail by examining the nature of ionic bond in sodium chloride, a typical ionic compound. The electronic configuration of sodium is 2, 8, 1. Only the last electron is important for bonding. If the sodium atom transfers its single valence electron to another atom, it acquires a positive charge (the resulting species has 10 electrons but still 11 protons, hence, it acquires the positive charge carried by the 11th proton). This positively charged species is called a *cation* (Fig. 3-16).

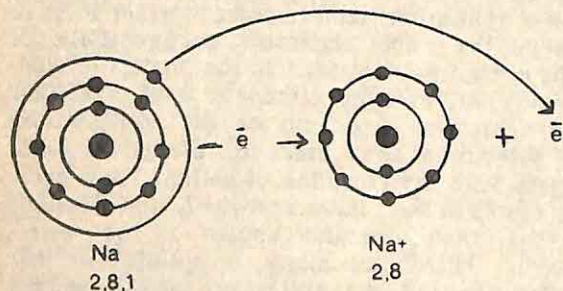


Fig. 3-16. Formation of sodium ion

The electronic configuration of chlorine is 2, 8, 7. The last seven electrons are valence

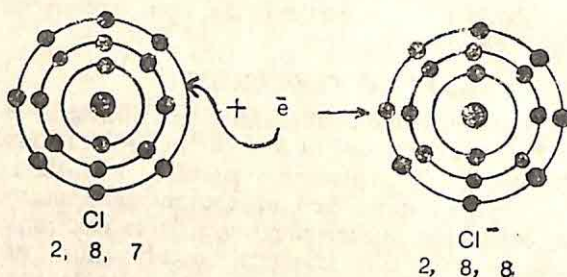


Fig. 3-17. Formation of chloride ion

electrons. If the chlorine atom accepts one electron from the other combining atom, it acquires the negative charge (the resulting species has 18 electrons but still 17 protons, hence, it acquires negative charge due to extra electron). This negatively charged species is called an *anion* (Fig. 3-17).

When sodium chloride forms, the sodium atoms lose electrons (forming sodium ion), transferring them to the chlorine atoms which in turn accept them forming chloride ions (Fig. 3-18).

As the sodium atom transfers its valence electron, it attains the electronic configuration of the neon atom (2, 8). As the chlorine atom accepts the electron, it attains the electronic configuration of the argon atom (2, 8, 8). The interaction between a sodium atom and a chlorine atom may be illustrated by electron-dot-representation (Lewis' structure). Figure 3-19 illustrates the Lewis' representation.

Note. Electrons shown by dots and small circles are identicals. They have been shown by different symbols just to indicate that they belong to different elements.

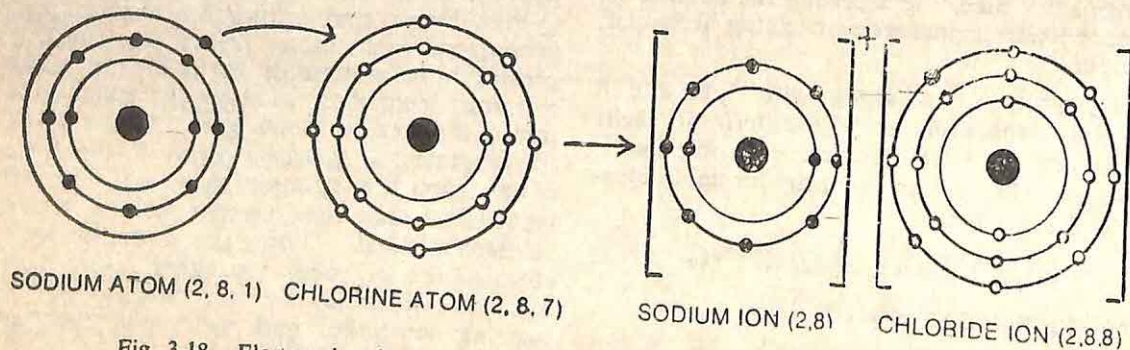


Fig. 3-18. Electrovalent interaction of sodium and chloride to form sodium chloride

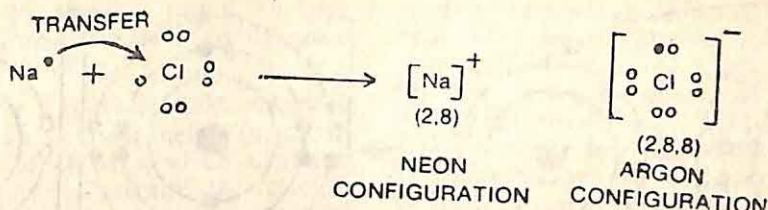


Fig. 3-19. Lewis' representation of sodium chloride

The cations and anions that are formed attract each other (by virtue of their opposite charges) to produce an infinite three dimensional crystalline lattice of sodium chloride.

Let us consider a few more examples.

Magnesium Chloride : Magnesium atom has two electrons in outermost shell. The two electrons are transferred to two chlorine atoms. In this process, magnesium ion (Mg^{2+}) and the two chlorine ions (Cl^-) acquire the stable electronic configuration of noble gases. The interaction has been portrayed in Fig. 3-20.

Lewis' representation of magnesium chloride is given in Fig. 3-21.

Calcium oxide : Calcium atom with electronic configuration 2, 8, 8, 2 loses two electrons to form Ca^{2+} ion (2, 8, 8). The two electrons lost by calcium are accepted by oxygen and becomes oxide ion, O^{2-} (2, 8). Thus the atoms attain stable electronic configurations. The diagram for the formation of calcium oxide is shown in Fig. 3-22.

The electron-dot representation for calcium oxide is given in Fig. 3-23.

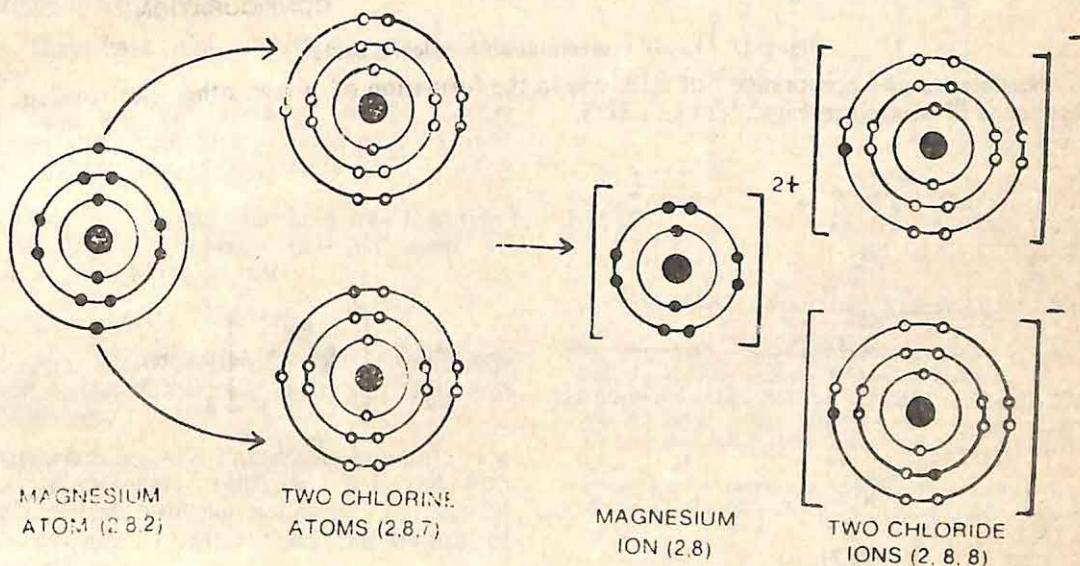


Fig. 3-20. Electrovalent interaction of magnesium and chlorine to form magnesium chloride

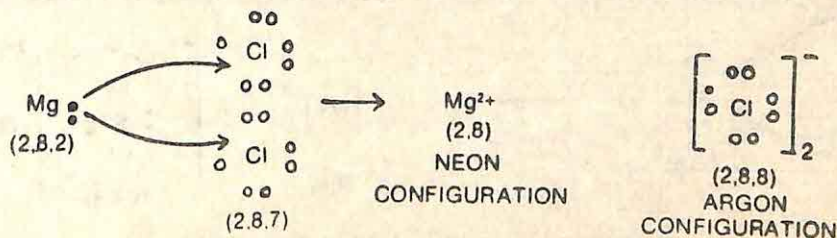


Fig. 3-21. Lewis' representation of magnesium chloride

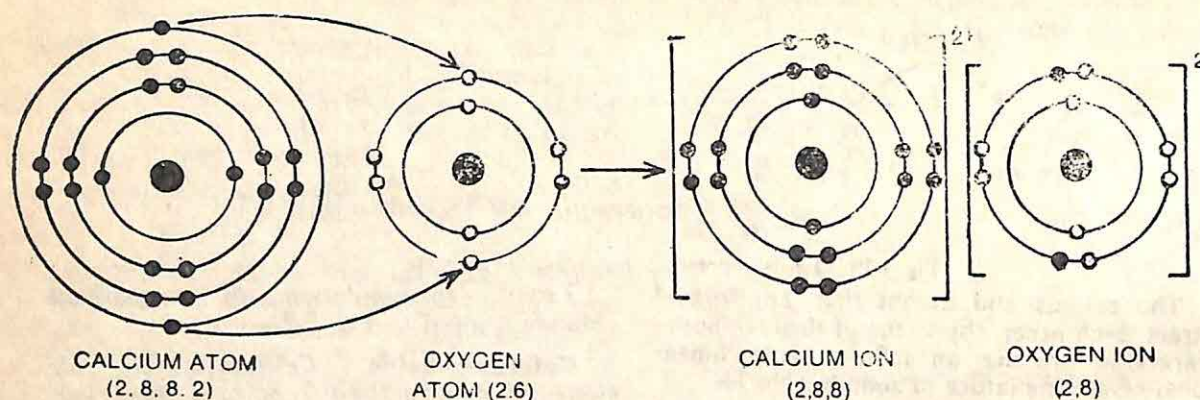


Fig. 3-22. Electrovalent combination of calcium and oxygen to form calcium oxide

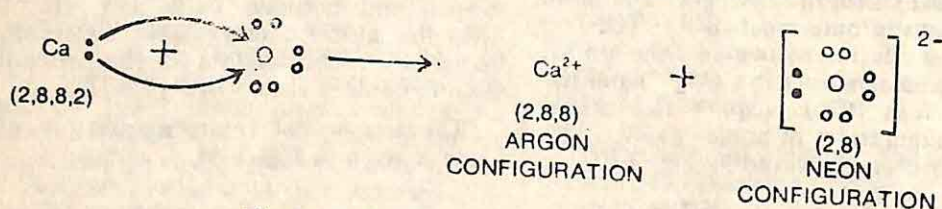


Fig. 3-23. Lewis' representation of calcium oxide

The transference and acceptance of electrons in the formation of a few other electrovalent compounds is illustrated in Figs. 3-24 and 3-25.

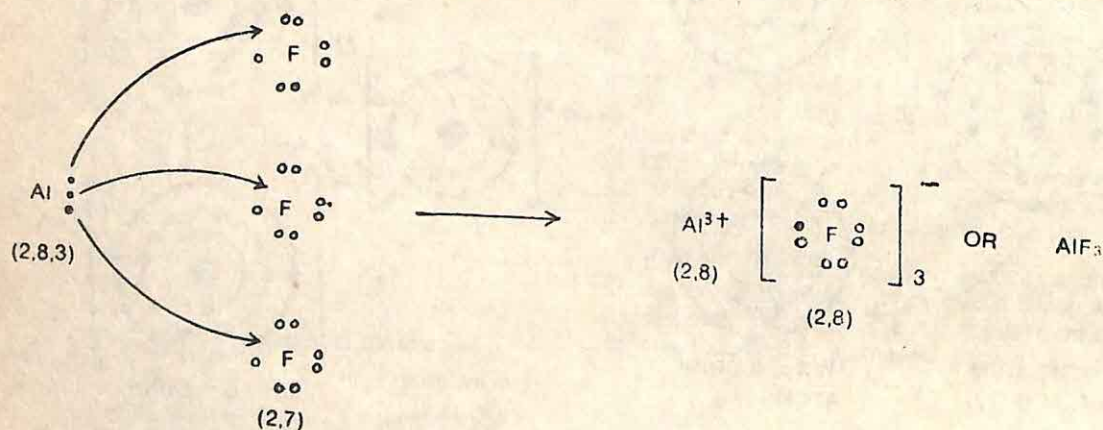


Fig. 3-24. Formation of aluminium fluoride

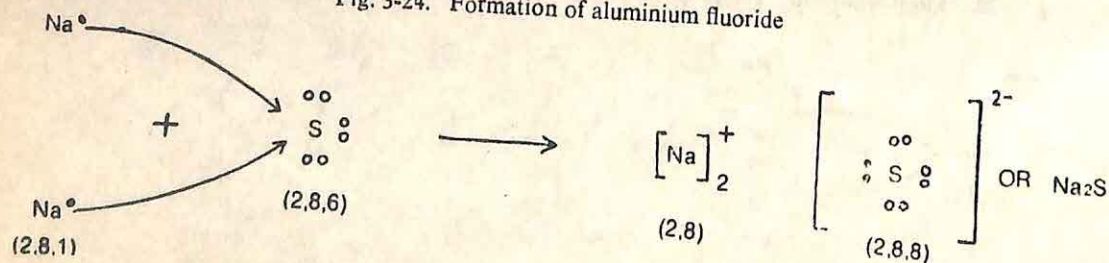


Fig. 3-25. Formation of sodium sulphide

Thus the number of electrons gained or lost by an atom of an element during chemical combination so as to attain stable configuration is called its *electrovalency*.

From the above it is evident that electronic configuration of an element helps to decide about the nature of elements which can form electrovalent bonds. Generally the element which can donate electrons easily, i.e., electro-positive (metallic) elements like, Li, Na, K, Be, Mg, Ca, etc. and the elements which can accept the electrons easily, i.e., electronegative (non-metallic) elements like F, Cl, O, S, etc. form ionic bonds and hence ionic solids.

Properties of electrovalent compounds

1. They contain oppositely charged ions only and have no molecule in them.

2. Their ions are held together by strong electrostatic forces of attraction. Hence these compounds are solids. Thus, the crystalline solids are a network of ions held together by electrostatic attraction.

3. They have high melting and boiling points.

4. They conduct electricity in the molten state and are, therefore, electrolytes. This is due to the presence of ions in the melt.

5. They are mostly soluble in water, but do not dissolve in organic solvents such as benzene, ether and acetone.

6. They ionize in solution.

7. Aqueous solutions of ionic compounds conduct electricity because ions are present in such solutions.

Experiment 3-1 Potassium sulphide is a typical alkali metal sulphide. It is put into water and the resulting solution conducts an electric current. Comment on the nature of compound.

Potassium sulphide is an electrovalent compound. Its formation is portrayed in Fig. 3-26.

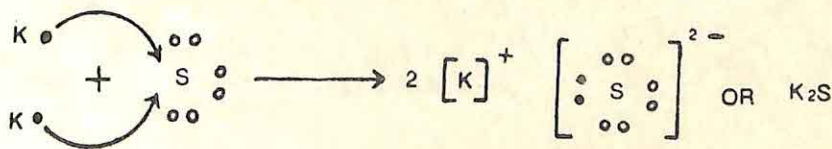


Fig. 3-26. Formation of potassium sulphide

Experiment 3-2 Electrovalent bonds confer electrical conductivity to substances. Take a solution of sodium chloride in water and dip the two electrodes in the salt solution. Connect these two electrodes to a battery via electric bulb as illustrated in Fig. 3-27. On pressing the key the bulb glows. This phenomenon confirms that the solution of NaCl furnishes ions which move freely and independently of one another. These ions conduct electric current. Similar compounds like MgCl_2 , KBr , CuSO_4 , etc. will also conduct electric current in aqueous solution.

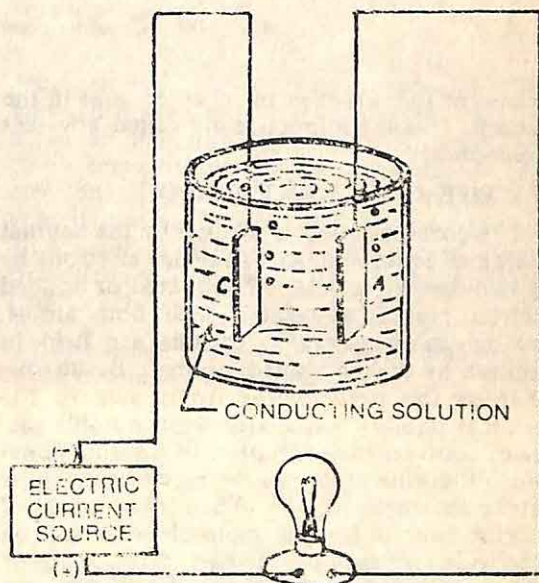


Fig. 3-27. Aqueous solution of ionic compounds conduct electric current. Current flows from the negative end of the source through the wire to the plate C. The current flows from C to A through the solution. From A to the positive terminal of the current source, the current flows through the wire. Conduction through the solution is signalled by the glowing bulb in the path.

Now if sodium chloride solution is substituted by sugar solution, chloroform or benzene, etc. the bulb does not glow. This is

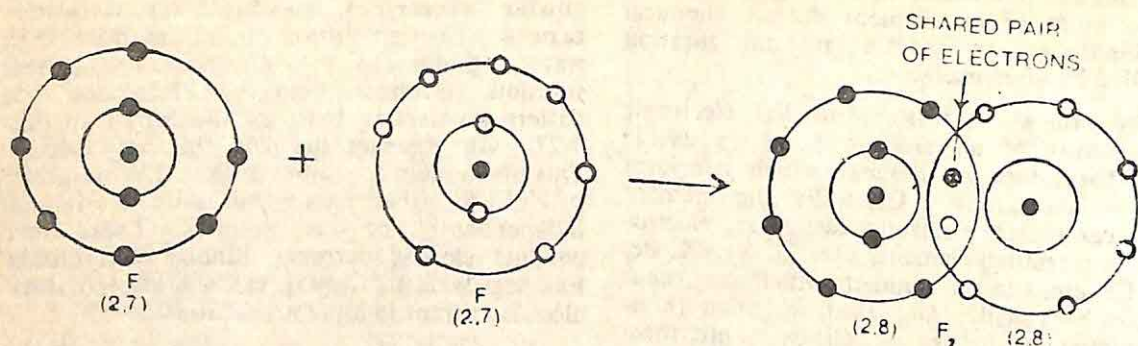


Fig. 3-28. Covalent combination of two fluorine atoms

because of the absence of charged ions in the solution. Such compounds are called covalent compounds.

3-15 THE COVALENT BOND

The covalent bond is formed by the mutual sharing of equal number of valence electrons by the two reacting atoms. The shared or bonded electron pair is associated with both atoms. One or more pair of electrons are held in common by the combined atoms. By sharing electrons, the participating atoms achieve the chemical stability associated with a noble gas. Let us consider the formation of fluorine molecule. Fluorine atom has seven electrons in its outermost shell (2, 7). When two atoms of fluorine unite to form a molecule, one electron is provided by each of the two fluorine atoms, fluorine molecule is formed in which both the fluorine atoms attain the stable octet electronic configuration as shown in Fig. 3-28.

The combination of two fluorine atoms may be illustrated below by electron-dot representation (Fig. 3-29)..

The pair of electrons that is shared between the two fluorine atoms constitute the covalent bond. The fluorine molecule with one shared electron pair (represented by a single line, —) will have a single bond. The remaining six pair of electrons that are not mutually shared are called *nonbonding electrons*.

Hydrogen molecule: Hydrogen atom contains one electron in its valence shell. In order to form H_2 molecule, both atoms share one electron each so as to create one shared pair of electrons. In the process, both the atoms attain the stable electronic configuration of helium (a duplet of electrons), see Fig. 3-30.

Hydrogen chloride. When one atom of hydrogen unites with one atom of chlorine, hydrogen attains a duplet of electrons and chlorine attains an octet of electrons by sharing a electron pair, one electron being given by each participants (Fig. 3-31).

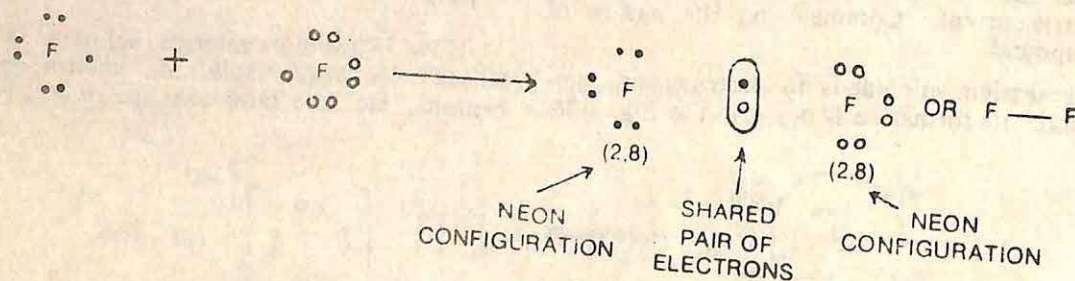


Fig. 3-29. Covalent bond formation in a fluorine molecule—a Lewis' representation

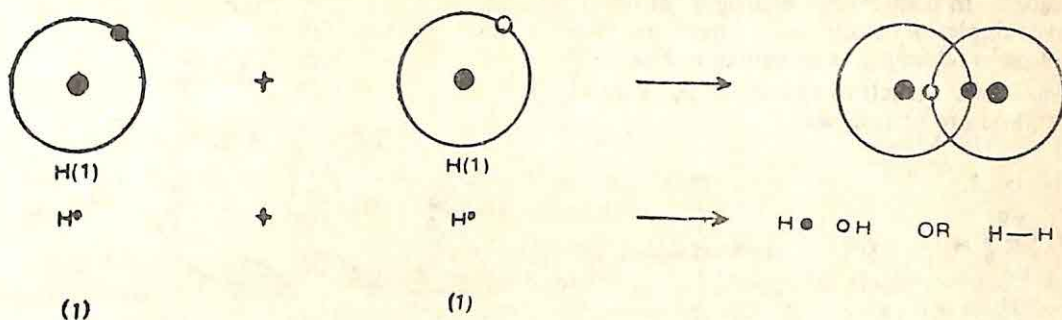


Fig. 3-30. Covalent bonding in a hydrogen molecule

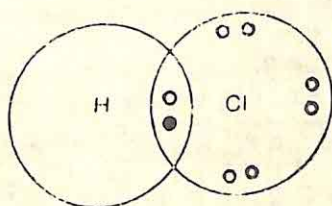
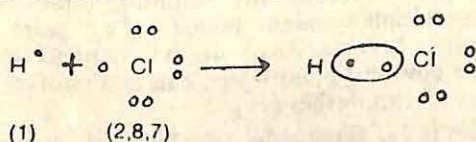


Fig. 3-31 Covalent bonding in a hydrogen chloride molecule

The electrons dot representation and structural formula of HCl are given below :



OR



Ammonia molecule : Ammonia has three atoms of hydrogen and one atom of nitrogen.

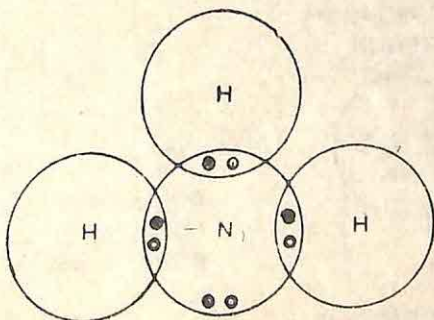
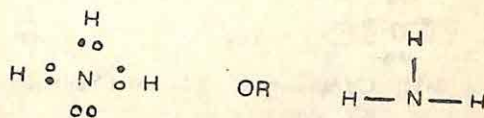


Fig. 3-32 Covalent bonding in ammonia molecule

Nitrogen with five electrons in its valence shell and hydrogen with one electron in its only shell attain an octet and duplet electronic configurations respectively. In the process, for each electron of hydrogen atom, nitrogen atom contributes an equal share. Thus, there are three pairs of electrons being shared between one nitrogen atom and three hydrogen atoms (Fig. 3-32).

The Lewis' structure and structural formula of ammonia are given below :



Methane molecule. A molecule has four hydrogen atoms and one carbon atom. The electronic configuration of carbon is 2, 4. Carbon shares its four electrons with hydrogen

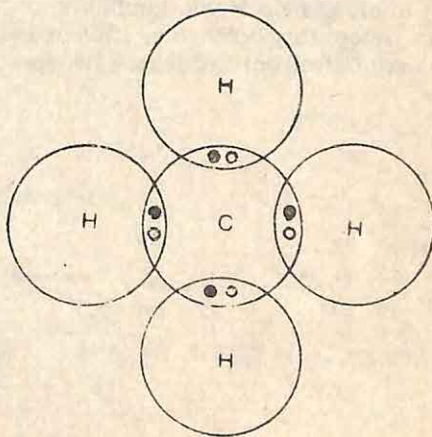
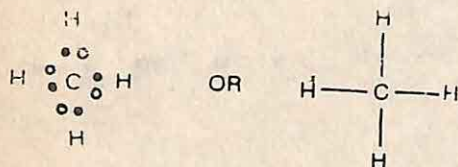


Fig. 3-33. Covalent bonding in methane

atoms to attain stable electronic configuration like neon. In turn every hydrogen atom also achieves duplet of electrons. There are four shared pairs of electrons as shown in Fig. 3-33.

The Lewis' structure and structural formula of methane are as follows :



The formation of a few other molecule through sharing of electrons is portrayed in Figs. 3-34 and 3-35.

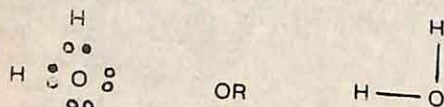
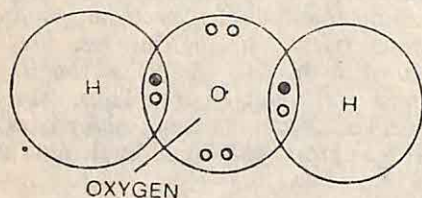


Fig. 3-34. Covalent bonding in water molecule

Multiple Covalent Bonds. In each of the examples discussed above, a single pair of electrons is shared between the constituent atoms in the given molecule. However, in some molecules, two or three pairs of electrons may be shared between atoms in order to attain a noble gas electronic configuration, and thus, to obey the octet rule. When two or three pairs of electrons are shared between two

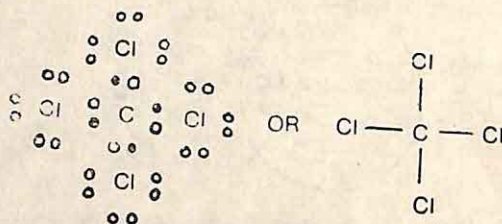
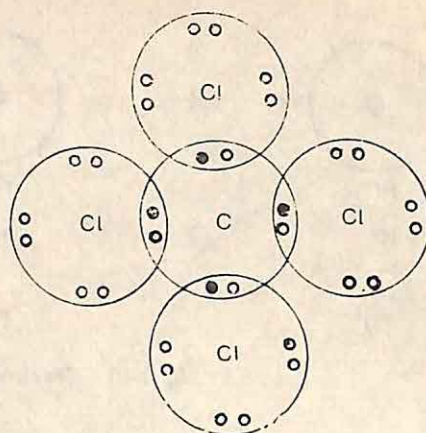


Fig. 3-35. Covalent bonding in carbon tetrachloride

atoms in a molecule, the resulting bonds are called multiple covalent bonds. Two pairs of electrons between two atoms constitute a double covalent bond which can be denoted by means of two dashes (=).

Similarly, three pairs of electrons between two atoms constitute a triple covalent bond which we denote by means of three dashes ($\equiv$).

Double and triple bonds occur in the Lewis' structures of oxygen and nitrogen molecules respectively. Each atom in a molecule of oxygen contributes two electrons to form two shared pairs of electrons as given in Fig. 3-36.

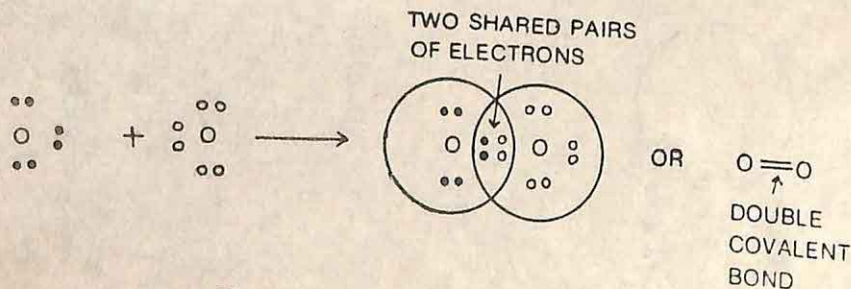


Fig. 3-36 Formation of oxygen molecule

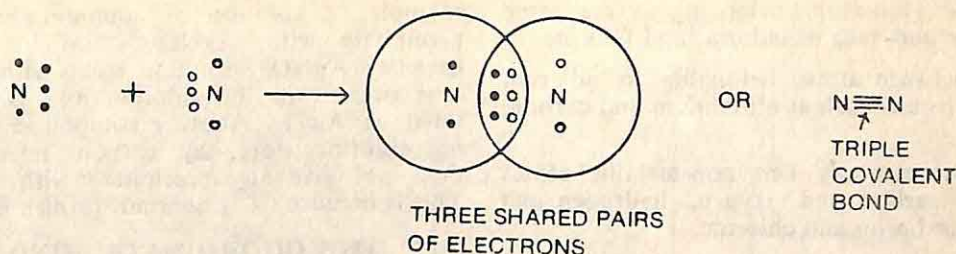


Fig. 3-37. Formation of nitrogen molecule

Similarly, each atom in a molecule of nitrogen shares three of its electrons with the other nitrogen atom to form a triple bond (Fig. 3-37).

The following covalent compounds also illustrate double bond and triple bond formation in the molecules.

In carbon dioxide, each of the two oxygen atoms shares two electron pairs with a carbon atom. Thus, each of the two oxygen atoms forms two covalent bonds and the carbon forms four covalent bonds (Fig. 3-38)

Ethylene and acetylene illustrate double bond and triple bond respectively. In ethylene molecule, each hydrogen atom is linked with the

carbon atom through a single covalent bond and both the carbon atoms are linked with each other through a double bond (3-39).

In acetylene molecule, each hydrogen atom forms one covalent bond with a carbon atom and each carbon atom forms a triple bond with the other carbon atom (Fig. 3-40).

Now the foregoing examples of covalent compounds reveal that the *covalency* of an element depends upon the number of electrons its one atom contributes for forming a covalent bond.

Covalent bonds are thus formed,

1. between identical atoms,

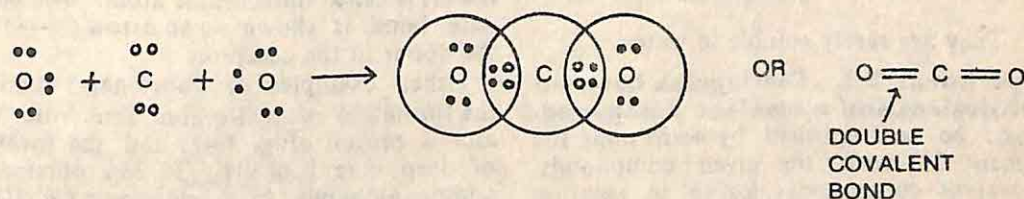


Fig. 3-38. Formation of carbon dioxide

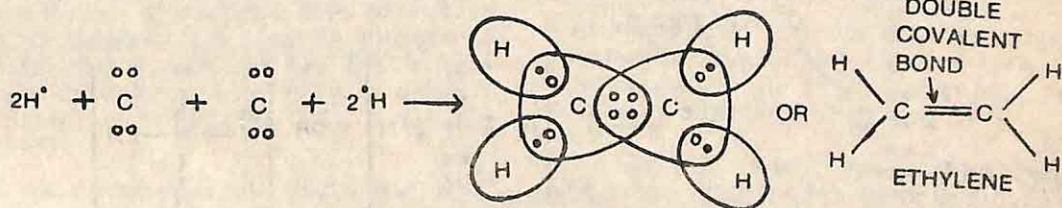


Fig. 3-39. Formation of ethylene

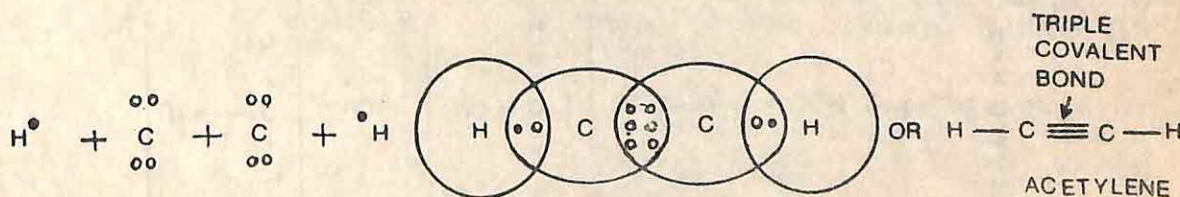


Fig. 3-40. Formation of acetylene

2. between atoms belonging to the same periodic group such as chlorine and fluorine,

3. between atoms belonging to adjacent periodic groups such as aluminium and carbon, and

4. between any two non-metallic atoms such as carbon and oxygen, hydrogen and chlorine or boron and chlorine.

Properties of covalent compounds

1. Covalent compounds consist of molecules and do not contain ions.

2. Simple covalent compounds are volatile liquids or gases because their molecules are electrically neutral and their intermolecular forces are much weak.

3. They have low melting and boiling points, however, covalent solids like diamond and graphite are exceptions.

4. They are non-electrolytes and do not conduct electric current when in molten state or dissolved in water.

5. They are readily soluble in organic solvents such as CCl_4 , CHCl_3 , CS_2 , acetone, etc.

6. They are rarely soluble in water.

Experiment 3-3. Distinguish between a electrovalent and a covalent compound. This can be accomplished by performing the experiment 3-2 with the given compounds. Electrovalent compounds ionize in solution whereas covalent compounds do not. For

example, a solution of common salt gives precipitate with AgNO_3 solution. This is because AgNO_3 solution reacts with the Cl^- ions present in the solution and is precipitated as AgCl . Another compound containing chlorine atom, say carbon tetrachloride does not give any precipitate with AgNO_3 . This is because CCl_4 does not furnish any ion.

3-16 THE COORDINATE BOND

A covalent bond results from the sharing of two electrons between the combining atoms. Each atom contributes one electron to form the shared pair. It is also, however, possible to form a covalent bond where both the electrons are contributed by one atom. This is called a *coordinate covalent bond* or simply *coordinate bond*. It is illustrated by the following examples :

Formation of the ammonium ion. The formation of NH_4^+ ion can be portrayed by Lewis' structures (Fig. 3-41). The lone pair of electrons on the nitrogen atom is shared with H^+ ion. The atom that supplies the electrons (here the nitrogen) is called the donor atom and the atom that accepts the electrons (here the H) is called the acceptor atom. The coordinate bond is shown as an arrow ($\rightarrow$) from the donor to the acceptor.

Other examples of coordinate bond are the formation of hydronium ion from water and a proton (Fig. 3-42) and the formation of deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion (obtained by adding ammonia to a solution of $\text{Cu}(\text{II})$ ions (Fig. 3-43).

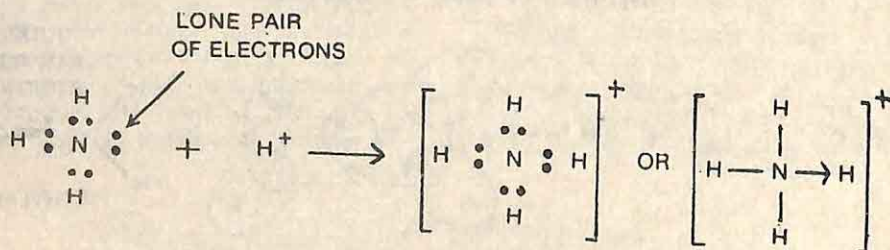


Fig. 3-41. Formation of a coordinate bond

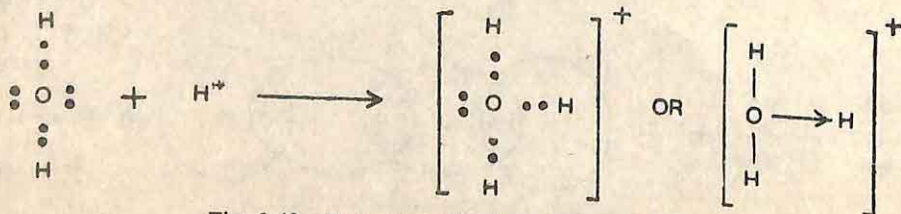
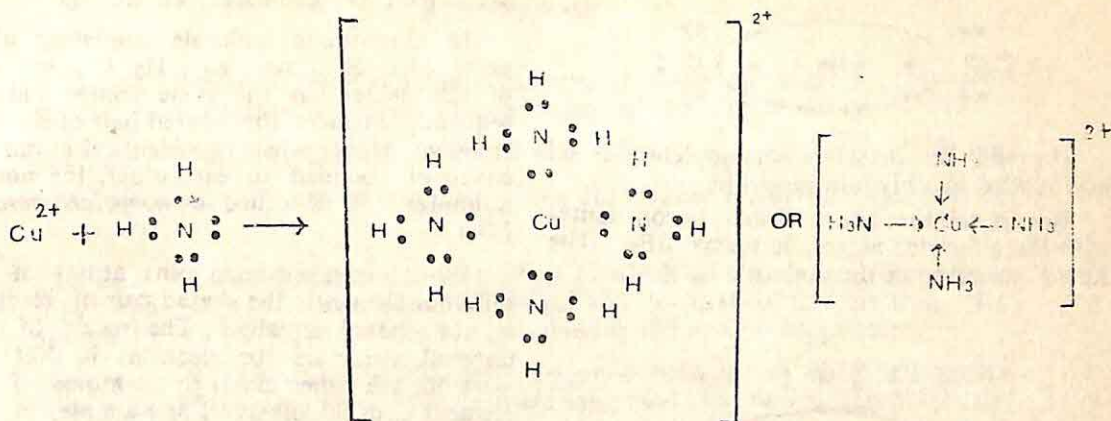
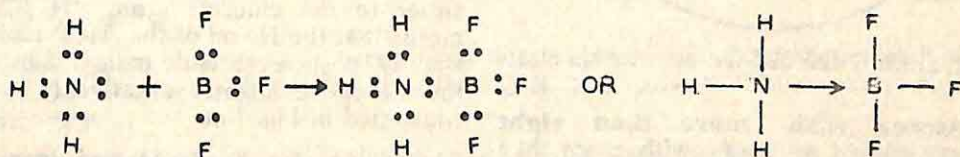
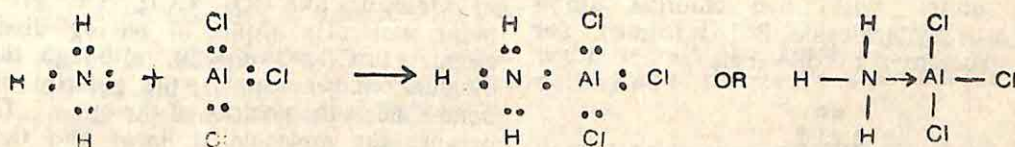
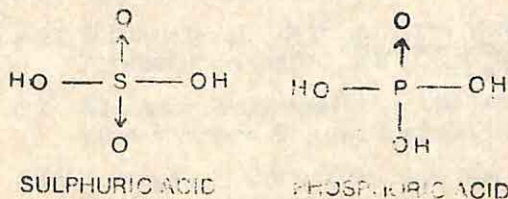


Fig. 3-42. Formation of hydronium ion, H_3O^+

Fig. 3-43. Formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ionFig. 3-44. Formation of the molecular complex, $\text{NH}_3 \cdot \text{BF}_3$ Fig. 3-45. Formation of the molecular complex, $\text{NH}_3 \cdot \text{AlCl}_3$

Two or more stable molecules can also combine through a coordinate bond to yield a molecular complex. For example, nitrogen in ammonia can donate its lone pair of electrons present in the outer shell to electron deficient compounds such as BF_3 (Fig. 3-44) and AlCl_3 (Fig. 3-45).

Certain compounds like sulphuric acid, phosphoric acid, etc. contain both covalent and coordinate bonds.

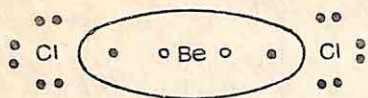


Exceptions to the octet rule

Although the octet rule is a very useful generalization in describing bonding, there are many substances for which it does not apply. We shall give two exceptions here :

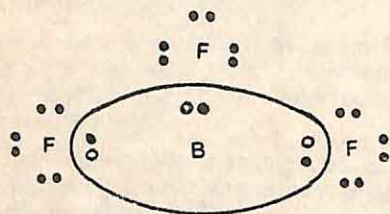
1. **Atoms with less than eight electrons.** When an atom with less than four electrons in its valence shell shares them to form covalent bonds, it may have less than an octet of electrons. Beryllium chloride and boron trifluoride can well illustrate this exception.

Beryllium chloride. Be in BeCl_2 has only two valence electrons and can, therefore, form a maximum of two ordinary covalent bonds with two Cl atoms. Thus the Lewis' structure of BeCl_2 is,



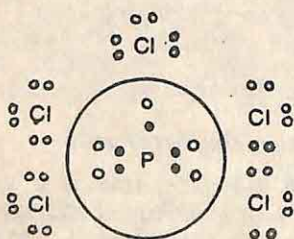
Around Be octet is incomplete; it is surrounded by only four electrons.

Boron trifluoride. When boron unites with three fluorine atoms, it forms BF_3 . The Lewis' structure of the molecule is,

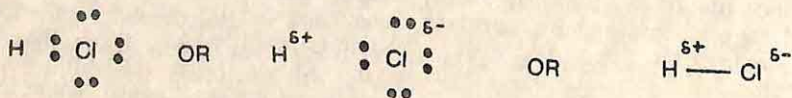


Boron atom is surrounded by only six electrons.

2. Atoms with more than eight electrons. When an atom with more than four electrons in its valence shall shares them to form covalent bonds it may have more than eight electrons. For example, when phosphorus unites with five chlorine atoms phosphorus pentachloride, PCl_5 is formed. The Lewis' structure of the molecule is,



Phosphorus' atom is surrounded by ten electrons.



3-17 POLAR COVALENT BOND

In a diatomic molecule consisting of the same type of atoms, e.g., H_2 , Cl_2 , etc. each of the nuclei has the same charge and consequently attracts the shared pair of electrons equally. Hence when two identical atoms are covalently bonded to each other, the bond is nonpolar. It is called a *nonpolar covalent bond*.

When a covalent bond joins atoms of two different elements, the shared pair of electrons is not shared equally. The result of this unequal attraction for electrons is that the electrons are pulled closer to the atoms of one element than the other. For example, in case of hydrogen chloride molecule, chlorine atom has more affinity for electrons than hydrogen atom. Therefore, the pair of electrons is held closer to the chlorine atom ($\text{H}:\text{Cl}$). This means that the H end of the HCl molecule is slightly positive (usually indicated by δ^+) and the Cl end is slightly negative (δ^-). This is illustrated in Fig. 3-46.

Such covalent bonds formed between dissimilar atoms are *polar covalent bonds* and such molecules are called *polar molecules*.

Molecules like CO_2 , CCl_4 , etc. are non-polar molecules inspite of having dissimilar atoms. In $\text{CO}_2(\text{O}=\text{C}=\text{O})$, although the individual bonds are polar, the polarity of one bond cancels the polarity of the other. This is because the molecule is linear and the pull offered by two oxygen atoms is equal. In CCl_4 , chlorine atoms are equidistant from the central carbon. The pull exerted by four chlorine atoms is equal in all respects. Hence, CO_2 , CCl_4 and similar other molecules are nonpolar in nature.

Fig. 3-46. The hydrogen chloride molecule – The covalent bond is polar.

KEY TERMS

- 3-1 **Electron.** A fundamental subatomic particle of which all matter is composed. It carries a negative electrical charge equal to 4.8×10^{-10} esu or 1.6×10^{-19} coulomb (1 unit). Its mass is 9.11×10^{-28} g (about $\frac{1}{1840}$ of the mass of the hydrogen atom). Electrons are distributed throughout the extranuclear part of the atoms.
- 3-2 **Proton.** A fundamental subatomic particle of which all atoms are composed. It carries a positive charge equal in magnitude to that of the electron. Its mass is 1.672×10^{-24} g. Protons are contained in the nucleus of an atom.
- 3-3 **Neutron.** A fundamental uncharged subatomic particle of which all atoms (except one of the isotopes of hydrogen) are composed. Its mass is approximately equal to that of a proton (1.675×10^{-24} g).
- 3-4 **Cathode rays.** A stream composed of electrons that move toward the anode in a cathode ray tube. They travel in straight lines and possess kinetic energy and momentum.
- 3-5 **Canal rays.** A stream of positive ions that move toward the cathode inside a cathode ray tube. They travel in straight lines and possess kinetic energy and momentum.
- 3-6 **Alpha particle (ray).** A radiation emitted from some radioactive substances and composed of particles having a charge of $+2$ and roughly four times as massive as a proton. An alpha particle is thus actually a helium nucleus (helium atom without its electrons i.e. ${}^4_2\text{He}^{2+}$). They move with high velocity but are not very penetrating because of their heavy mass.
- 3-7 **Nucleus.** The positively charged region at the centre of an atom occupied by protons and neutrons. It accounts for essentially all of the atom's mass but for only a very small fraction of its volume.
- 3-8 **Nucleons.** The nuclear particles, i.e., both neutrons and protons present in an atomic nucleus are known as nucleons.
- 3-9 **Atomic number.** The number of protons in an atomic nucleus is referred to as the atomic number. Thus, an atom with an atomic number of 8 may be thought of as containing 8 protons in its nucleus. In a neutral atom, the atomic number is also the number of extranuclear electrons in the atom.
- 3-10 **Mass number.** The total number of nucleons (protons and neutrons) in an atomic nucleus is called mass number. The mass number is always a whole integer. The mass number of an atom is its atomic number plus the number of neutrons in its nucleus. Not all atoms of an element have the same mass number.
- 3-11 **Orbit.** The path of the electrons around the nucleus represents orbit.
- 3-12 **Energy level.** It refers to the definite quantities of energy allowed in atoms depending on the location of electrons.
- 3-13 **Electron configuration.** The arrangement of electrons in the orbits of an atom is termed electron configuration.
- 3-14 **Isotopes.** Atoms that have the same atomic number but different mass numbers, i.e., atoms that have the same number of protons but different number of neutrons are called isotopes.

- 3-15 **Valence electrons.** Electrons present in the outermost energy level of an atom. Valence electrons take part in chemical bonding and chemical reactions.
- 3-16 **Chemical bond.** The force of attraction that binds the atoms together in a molecule is called a chemical bond.
- 3-17 **Inertness (of noble gases).** The inertness of the noble gases is ascribed to their stable electronic configuration.
- 3-18 **Ions.** An atom or molecule that carries a positive or negative charge because of loss or gain of electrons.
- 3-19 **Anion.** An ion which carries negative charge.
- 3-20 **Cation.** An ion which carries positive charge.
- 3-21 **Ionic bond.** The electrostatic force of attraction that mutually attracts ions of opposite charge. It is established by the transfer of electrons from one atom (electropositive) to another (electronegative).
- 3-22 **Covalent bond.** A chemical bond formed by the sharing of electron pairs between two atoms (non-metallic atoms).
- 3-23 **Lewis' structure or formula.** A means of displaying a molecule or an ion. Here, dots, X's and empty circles are used to represent electrons.
- 3-24 **Octet rule.** For atoms other than hydrogen in a molecule, the total number of shared and unshared electrons should be eight in the outermost shell which depicts the stable electronic configuration of the noble gases.
- 3-25 **Single bond.** A covalent bond formed by the sharing of one electron pair between two atoms.
- 3-26 **Double bond.** A covalent bond formed by the sharing of two electron pairs between two atoms.
- 3-27 **Triple bond.** A covalent bond formed by the sharing of three electron pairs between two atoms.
- 3-28 **Coordinate covalent bond.** A covalent bond consisting of a pair of shared electrons, both given by one of the atoms it joins.
- 3-29 **Bond polarity.** A measure of the unequal sharing of electron pairs between bonded atoms, so that one end of the bond is negative with respect to the other end.
- 3-30 **Polar covalent bond.** A bond in which the electronic charge is not symmetrically distributed between its two atoms.
- 3-31 **Structural formula.** A depiction of a molecule or an ion in which atoms are attached to one another. Dash is used to show the attachments or linkages.

UNIT THROUGH EXERCISES

3-1 Point out the wrong statements of the following:

(i) All atoms of a given element contain the same number of protons in their nuclei and electrons outside their nuclei.

(ii) The addition of neutrons to the nucleus of an atom would increase the mass number.

(iii) The atomic number of an element accounts for the number of positive charges in the nucleus.

- (iv) Isotopes of an element differ in the number of neutrons.
- (v) Electrons move in definite energy levels.
- (vi) The reactivity of an atom is determined by its electronic configuration.
- (vii) Ionic compounds are formed by the transfer of electrons, whereas covalent compounds are formed by the sharing of electrons.
- (viii) The shared pair of electrons is always shared equally in a covalent compound.
- (ix) Octet rule is always helpful in explaining the structures of various molecules.
- (x) Hydrogen chloride is a polar molecule.

Ans. Statements (viii) and (ix) are not correct.

3-2 (a) Which of the following electronic configurations represent a noble gas, oxygen and potassium?

- (i) 2, 8, (ii) 2, 8, 1, (iii) 2, 6, (iv) 2, 8, 8, 1.

Ans. (i) represents a noble gas.

(iii) represents oxygen.

(iv) represents potassium.

(b) Consider the following table :

	Proton	Neutron	Electron
A	18	22	18
B	17	18	17
C	7	7	7
D	9	10	9
E	17	20	17

Choose from the table the letters (A to E) that represents (i) a pair of isotopes, (ii) an element having a mass number of 19, (iii) an atom of a noble gas, and (iv) an element with 5 electrons in the valence shell.

Ans. (i) B and E are isotopes.

(ii) D is an element with mass number 19.

(iii) A is a noble gas.

(iv) C is an element with 5 electrons in the valence shell.

3-3 (a) What type of bonding would you expect in the following sets when two atoms A and B with the given electronic structures combine with each other?

(i) A=2, 8, 1

B=2, 7

(ii) A=2, 8, 8, 2

B=2, 6

(iii) A=2, 8, 7

B=2, 8, 7

Ans. (i) Ionic bonding

(ii) Ionic bonding

(iii) Covalent bonding

(b) In forming a compound XY, atoms of X lose one electron each while the atoms of Y acquire one electron each. Predict the nature of the compound and give its two properties.

Ans. Compound XY is ionic in nature. Its ions are held by strong electrostatic forces of attraction. It is soluble in water].

3-4 (a) Assign electrons in the following :

(i) M-shell of an atom,

(ii) Element with 26 protons,

(iii) Element with atomic number 20,

and (iv) Sodium.

Ans. (i) M is numbered as 3rd shell. On the basis of $2n^2$, M will have 18 electrons, (ii) 26 electrons, (iii) 20 electrons, and (iv) 11 electrons.

(b) Assume that one electron has been removed from each of the atoms : Li, Na, K to form Li^+ , Na^+ and K^+ and that one electron has been added to F and Cl atoms to form F^- and Cl^- . Give the electronic configurations for all these ions. Mention the noble gases which can represent these electronic configurations.

Ans. $\text{Li}^+=2$,	Represents	He
$\text{Na}^+=2, 8$	Represents	Ne
$\text{K}^+=2, 8, 8$	Represents	Ar
$\text{F}^-=2, 8$	Represents	Ne
$\text{Cl}^-=2, 8, 8$	Represents	Ar

(c) Give answers to each in one or two words or a sentence.

(i) What is the number of neutrons in an element whose mass number and atomic number are 18 and 7 respectively?

(ii) If both K and L shells of an atom are full, what is the total number of electrons contained in them?

(iii) What is Rutherford's atomic model?

(iv) In what way cathode rays are different from canal rays ?

(v) What is nucleus ?

(vi) Does the atomic number of an element change when its atoms form ions ?

(vii) The atomic number of chlorine is 17. What is the number of electrons in Cl^- ?

(viii) An element has three electrons in the M shell. What is the atomic number of the element ? Name the element.

(ix) Two atomic species say A and B have 6 protons each. But A and B have 6 and 8 neutrons respectively. What is the relation between the two ?

(x) Why is the ratio e/m for positive rays different for different gases ?

Ans. (i) 11 neutrons

(ii) 10 electrons

(iii) It consists of a positive nucleus around which electrons are revolving.

(iv) Cathode rays are composed of negatively charged particles (electrons) while canal rays are composed of positively charged ions.

(v) The small positively charged central part of an atom is called nucleus.

(vi) Atomic number of an element does not change when it forms ions because the number of protons remains the same.

(vii) 18 electrons

(viii) 13 ; Aluminium

(ix) Isotopes of carbon, $^{12}_6\text{C}$, $^{14}_6\text{C}$

(x) Positive rays are produced by the loss of electrons from gaseous atoms, and hence, different gases would produce positive rays of different masses, and thus of different e/m values.

3-5 (a) Which of the properties of ionic compounds given below is not correct ?

(i) Ionic solids permit the passage of electric current.

(ii) Melt permits the passage of electric current.

(iii) Have high melting and boiling points.

(iv) Soluble in polar solvents.

Ans. Statement (i) is not correct.

(b) Which electrons take part in bond formation ?

Ans. Valence electrons present in the outer most shell.

(c) Which of the following pairs do you expect to be a polar molecule ?

(i) CCl_4 or HCl

(ii) CO or CO_2

Ans. (i) HCl (ii) CO

(d) Choose the ionic compounds of the following compounds :

(i) Cl_2 , (ii) MgCl_2 ,

(iii) AlF_3 , (iv) NH_3 ,

(v) CO_2 , (vi) CH_4 ,

(vii) MgO , (viii) CaCl_2 .

Ans. Ionic compounds : (i) MgCl_2 ,

(iii) AlF_3 , (vii) MgO and (viii) CaCl_2

(e) (i) If X and Y have the following electronic configurations, how many atoms of the element X will combine with one atom of Y ?

$X=2, 8, 7$, $Y=2, 4$

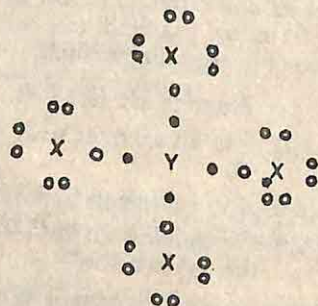
(ii) Give the Lewis' structure of the compound.

(iii) What would be nature of the bond formed between X and Y ?

(iv) Name the compound.

Ans. (i) Four atoms of X will unite with one atom of Y .

(ii)



(iii) Covalent bond

(iv) Carbon tetrachloride

Multiple Choice Questions

3-6 Put a tick (✓) mark against the suitable choice :

- (i) Which one of the following descriptions of cathode rays is not correct ?
 (a) move in a straight line.
 (b) depend upon the nature of gas used in a discharge tube.
 (c) cast shadow of the solid object placed in their path.
 (d) are deflected towards the positive pole of the magnetic field.
- (ii) Isotopes of an element have :
 (a) same number of neutrons.
 (b) same atomic number
 (c) same atomic mass.
 (d) same number of protons.
- (iii) Which of the following arrangements of electrons represents aluminium ?
 (a) 2, 8, 1 (b) 2, 8, 2
 (c) 2, 8, 3 (d) 2, 8, 4.
- (iv) Which of the following statements is not correct for Bohr's model of atom ?
 (a) The nucleus of an atom is situated at its centre.
 (b) The electrons move in circular orbits.
 (c) Electrons can jump from one orbit to another.
 (d) An electron neither loses nor gains energy in jumping from one orbit to another.
- (v) Which of the following statements is not correct ?
 (a) The whole mass of an atom is concentrated in the nucleus.
 (b) Valence electrons are involved in chemical bond formation.
 (c) Atomic number represents the number of protons contained in the nucleus.
 (d) Both deuterium and tritium contain 2 protons each.
- (vi) Two atoms A and B with electronic configuration 2, 8, 8, 2 and 2, 8, 7 respectively form a molecule. What will be the formula of the molecule ?

- (a) AB (b) AB₂
 (c) A₂B (d) BA.

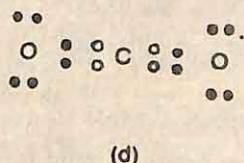
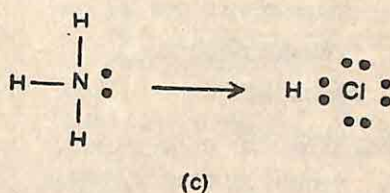
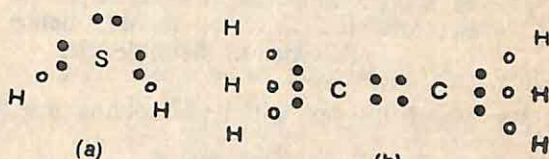
(vii) Which of the following illustrates the bonding in O₂ ?

- (a) Two electrons are shared.
 (b) Four electrons are shared.
 (c) Electron is transferred.
 (d) Electrons are not shared.

(viii) A cation is formed :

- (a) by sharing a pair of electron.
 (b) by donating an electron.
 (c) by accepting an electron.
 (d) by accepting a proton.

(ix) Which of the following electron dot structures is not correct ?



(x) Electrovalent compounds conduct electricity when dissolved in water because :

- (a) their ions are free in solution.
 (b) their ions form aggregates in solution.
 (c) the crystal structure persists.
 (d) electrons are supplied by water.

Ans. (i) (b), (ii) (b), (iii) (c), (iv) (d),
 (v) (d), (vi) (c), (vii) (b), (viii) (b),
 (ix) (b), (x) (a)

3-7 Fill in the blanks in the following :

- (1) The maximum number of electrons in an energy level is given by the formula
- (2) The and charge of an atom are concentrated in its nucleus.
- (3) Cathode rays consist of charged particles while canal rays are charged.
- (4) The neutral atomic particles, the were discovered by and are located in the of the atoms.
- (5) If a neutral atom contains 16 electrons, it will contain
- (6) compounds are formed by complete transfer of
- (7) In a HCl molecule, the shared pair of electrons is shared, hence develops in the molecule.
- (8) Mutual sharing of electrons between two atoms gives rise to bond.
- (9) A bond in which one atom donates both electrons of the shared pair is called a covalent bond.
- (10) HF is more polar than HCl, so it should have melting and boiling points than HCl.

Ans. 1. $2n^2$

2. mass, positive
3. negatively, positively
4. neutrons, Chadwick, nucleus
5. sixteen protons
6. ionic, electron
7. not equally, polarity
8. covalent
9. coordinate
10. higher

3-8 Match the descriptions in column B with the terms/statements in column A :**Column A**

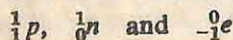
1. Mass of an atom
2. Valence electrons
3. Isotopes
4. Electrons
5. Atomic number
6. Mass number
7. Ionic compound
8. Carbon dioxide
9. Covalent compound
10. Chloroform

Column B

1. Nuclei that differ in their masses
2. Nucleus
3. Formed by sharing of electrons
4. Take part in chemical bonding
5. A covalent compound
6. Extranuclear region
7. Ions are held by strong electrostatic forces of attraction
8. Number of protons in the nucleus
9. Number of protons and neutrons in the nucleus
10. A nonpolar molecule.

REVIEW QUESTIONS

3-1 (a) What do you understand by the following symbols ?



(b) Give the location, mass and charge of the three fundamental particles.

3-2 (i) A neutral atom has electronic structure 2, 8, 6. Deduce as many of the following as you can from this information only

- (a) the atomic number of the element,
- (b) the atomic weight of the element,

- (c) the number of valence electrons, and
 (d) the name of the element.
- (ii) Name the elements that correspond to each of the following electronic configurations :
 2, 2 ; 2, 8 ; 2, 5 ; 2, 8, 6 ; 2, 8, 8, 2.
- 3-3 (a) Write the electronic configurations of Li, Na and K. In what ways are they similar ?
 (b) Name isotopes of hydrogen, carbon and chlorine. Give the different types of particles present in them.
- 3-4 Complete the following table :

Element	Atomic number	Protons	Neutrons	Electrons	Mass number
A	20	—	—	—	40
B	—	4	—	—	9
C	11	—	—	—	23
D	—	6	6	—	—
E	17	—	18	—	—
F	1	—	—	—	1

- 3-5 From the table given below give the following information :
- (i) which item has got metallic nature ?
 (ii) which item represents a metallic ion ?
 (iii) which two items are isotopes ?
 (iv) which items are non-metallic in nature ?
 (v) which item is a non-metallic ion ?
 (vi) which items represent noble gases ?
 (vii) which item represents a hydrogen ion ?

Item	Protons	Neutrons	Electrons
A	10	10	10
B	2	2	2
C	1	0	0
D	12	12	10
E	15	16	19
F	19	20	19
G	17	18	18
H	15	17	15

- 3-6 (a) Write the electronic configurations of Li, Na, Mg, Si, Cl and Ca. Will these atoms form covalent or ionic compounds ? Why ?
 (b) From the electronic configurations of the following atoms predict the most likely charge the ions will assume : Na, F, Al, S, Be and Ar.

- 3-7 (a) Indicate the nature of bonding in the following compounds : MgO, CaS, NaBr, CHCl₃, CCl₄, HCl, ICl, H₂O and NaOH.
 Also list the polar compounds.
- (b) Draw Lewis' structures for the following compounds : MgCl₂, NH₃, CaO, CHCl₃, H₂SO₄, NaCl.
- 3-8 What are cathode rays ? Describe experiments to show their properties and to prove that they are composed of electrons.
- 3-9 Suggest an experiment to prove the existence of positively charged particles in the atom. Give four important properties of them.
- 3-10 What is neutron ? Give the details of the experiment which led to the discovery of neutron.
- 3-11 What evidence led us to believe that there exists a nucleus in each atom ? Explain in detail.
- 3-12 Describe an experiment which leads us to infer that :
 (a) the whole mass of an atom is centred in the nucleus of the atom, and
 (b) the central part of the atom, i.e., the nucleus has all the positively charged particles.
- 3-13 What are the drawbacks of Rutherford's atomic model ? How did Bohr improve upon the Rutherford's atomic model ?
- 3-14 Describe the present concept of an atom. How are electrons arranged in an atom ? Give the salient features of the scheme which govern the arrangement of electrons.
- 3-15 What are isotopes ? Why do isotopes have similar chemical properties ? Give three examples.
- 3-16 There is no electric charge on the atom of the element in spite of the fact that every atom has negatively charged particles. Comment.
- 3-17 (a) List the various characteristics of ionic and covalent compounds.
 (b) Which of the many electrons are involved in the bond formation ? Explain.
- 3-18 (a) Differentiate between electrovalency and covalency.
 (b) Explain the formation of cations and anions in electrovalent compounds.

UNIT 4

Periodic Classification of Elements



Dimitri Iyanovitch Mendeleev
(1834–1907)

Mendeleev's periodic law and compilation of the periodic table of elements in 1869, systematized knowledge of the properties of the elements and predicted the existence of several then undiscovered elements.

Learning Objectives

At the completion of this unit, you should be able to :

1. Emphasize the need of classifying elements.
2. Describe the early attempts to classify the elements.
3. Explain what is meant by the term periodicity as applied to the elements.
4. Describe the criterion of classifying elements adopted by Mendeleev.
5. State the periodic law and understand its significance.
6. Sketch the arrangement of groups and periods on the periodic table.
7. Illustrate the position of related groups of elements on the periodic table.
8. Put forward the modern basis of classifying elements.
9. Give the merits and demerits of the long form of periodic table compared to improved form of Mendeleev's periodic table.
10. Describe the variation in metallic nature, atomic radius, density, melting and boiling points in the periodic table.

4-1 INTRODUCTION

Today 106 elements are known and with the steady development of new ways of synthesising elements this number is bound to continue increasing. Their systematic study would present quite a formidable problem but for the fortunate fact that they could be grouped together in families based on certain similarities and regularities in their properties.

During the 19th century, many elements were discovered along with detailed knowledge of their physical and chemical properties. The elements differed from one another in many of their properties. Some were soft and powdery, while others were hard and shiny; some were gases and others were liquids at ordinary temperatures, and so on. It was also found that certain elements resembled with one another in some respects. The compounds formed by element combinations revealed both some resemblances and differences among the elements. It was found that sodium and potassium metals have many similarities in their properties (Table 4-1).

Similarly, alkaline earth metals, Ca, Sr, and Ba were found to show a marked resemblance. They show a valency of 2. Their oxides, hydroxides, carbonates, etc. show bivalency. Their oxides react with water to form hydroxides, $M(OH)_2$. Their carbonates are soluble in water and on heating give same products, i.e., $MO + CO_2$.

Fluorine, chlorine, bromine and iodine were found to show similarity in properties to a large extent. They are very reactive non-metals and exist in the combined state. Under normal conditions they exist as diatomic molecules in which the atoms are held together with covalent bonds. All halogens react with

hydrogen under different conditions and form covalent hydrohalides which are soluble in water and produce aqueous solutions known as hydrofluoric, hydrochloric, hydrobromic and hydroiodic acids. They react with active metals like Na, Mg, etc., forming halides which are electrovalent in nature. They exhibit univalency in all these compounds.

Nitrogen and phosphorus; oxygen and sulphur; etc. were found to show a significant chemical resemblance. Both the nitrogen and phosphorus show trivalency (e.g., NH_3 , PH_3) and pentavalency (e.g., N_2O_5 , P_2O_5 or P_4O_{10}) in their compounds. Both the oxides (N_2O_5 or P_4O_{10}) are strongly acidic and on reacting with water form acids (HNO_3 and H_3PO_4). Their halides (NX_3 and PX_3) are covalent in nature. Thus, certain similarities and regularities do exist among elemental substances, and these serve as the basis for a detailed and very useful classification of the elements.

It was from attempts to relate the chemical and physical properties of the elements and their compounds to their atomic masses that the periodic table was born.

4-2 EARLY ATTEMPTS FOR CLASSIFICATION OF ELEMENTS

Elements were, first of all, divided by Lavoisier into two groups, (i) metals, and (ii) non-metals. Elements with metallic lustre, malleability, ductility, good conductivity of heat and electricity were identified as metals whereas the remaining elements were known as non-metals. This classification did not prove to be very useful as some elements, called metalloids, exhibited some properties characteristic of both metals and non-metals. It was also attempted to classify the elements on the basis of their acidic and basic character. This method also proved unsatisfactory as no clear

Table 4-1

Property	Sodium, Na	Potassium, K
Valency in their compounds	Monovalent	Monovalent
Reaction with water	Reacts	Reacts
Nature of oxides	Na_2O (basic)	K_2O (basic)
Nature of hydroxides	NaOH, a strong alkali	KOH, a strong alkali
Nature of carbonates	Na_2CO_3 (alkaline), soluble in water	K_2CO_3 (alkaline), soluble in water

distinction could be made. It varied according to experimental conditions.

Following the development of atomic theory and the determination of the atomic masses (or weights) of a large number of elements with a reasonable accuracy, attempts were made to find a relationship between atomic weight which seemed to be fundamental, and chemical properties.

In 1815, William Prout suggested that all the elements were formed by the simple aggregation of hydrogen atoms keeping in view that all atomic weights were whole number multiples of the atomic weight of hydrogen. However, soon it was found that most of the elements possessed fractional atomic weights. The hypothesis was, thus not taken seriously. But no sooner had Prout's proposal been abandoned than the attempts of several other scientists to order and classify the elements appeared.

(a) Dobereiner's Triads

In 1829 J.W. Dobereiner arranged closely related elements in groups of three, *i.e.*, triads, where the atomic weights of the middle element were nearly the arithmetic mean of the other two. Some triads are listed in Table 4-2.

Little attention was paid to this observation at that time as some other groups of triads such as arsenic, antimony, bismuth and zinc, cadmium, mercury did not conform to the law.

(b) Newlands' Law of Octaves

The next attempt for classifying the elements was made by John Newlands (1864). He arranged elements according to increasing atomic weights. Starting with any given element, every eighth element resembled in

properties to the first, similar to the repetition of musical notes in scales of eight. He called this generalization the *law of octaves*. His scheme was somewhat as follows :

Li	Be	B	C	N	O	H
Na	Mg	Al	Si	P	S	F
K	Ca	Cr	Ti	Mn	Fe	Cl

The scheme failed on attempting to extend it beyond calcium. Elements beyond calcium appeared out of place in Newlands' scheme. This happened because many elements had not been discovered at that time and Newlands did not provide any blank space for them in his scheme. Newlands' rule did not hold true at all. Indeed his ideas met with ridicule from other scientists, one of whom suggested that it would be just as valuable to arrange the elements in alphabetical order. The importance of Newlands' contribution was finally acknowledged in 1887, when he was awarded the Davy Medal by the Royal Society.

Mendeleev and others developed further the idea of Newlands. Newlands deserves credit for recognizing the periodic recurrence of properties based on increasing atomic weight—an idea that formed the basis for later classifications of the elements.

(c) The Periodic Table

(i) **The Periodic Law.** Dimitri Ivanovitch Mendeleev and Julius Lothar Meyer, working independently developed a classification scheme of the elements known at that time. Almost simultaneously, in 1869, these men published their versions of the classification. Meyer's work was based mainly on physical properties such as atomic volume, fusibility and brittleness. Mendeleev's developed his ideas about the periodicity of the elements by comparing the chemical properties of the elements and

Table 4-2. Dobereiner Triads

Triad				Mean atomic weight
Element	Lithium	Sodium	Potassium	
Atomic weight	7	23	39	$\frac{7+39}{2} = 23$
Element	Calcium	Strontium	Barium	
Atomic weight	40	87.6	137.4	$\frac{40+137.4}{2} = 88.7$
Element	Chlorine	Bromine	Iodine	
Atomic weight	35.5	80	127	$\frac{35.5+127}{2} = 81.25$
Element	Sulphur	Selenium	Tellurium	
Atomic weight	32.2	79.3	129.2	$\frac{32.2+129.2}{2} = 80.7$

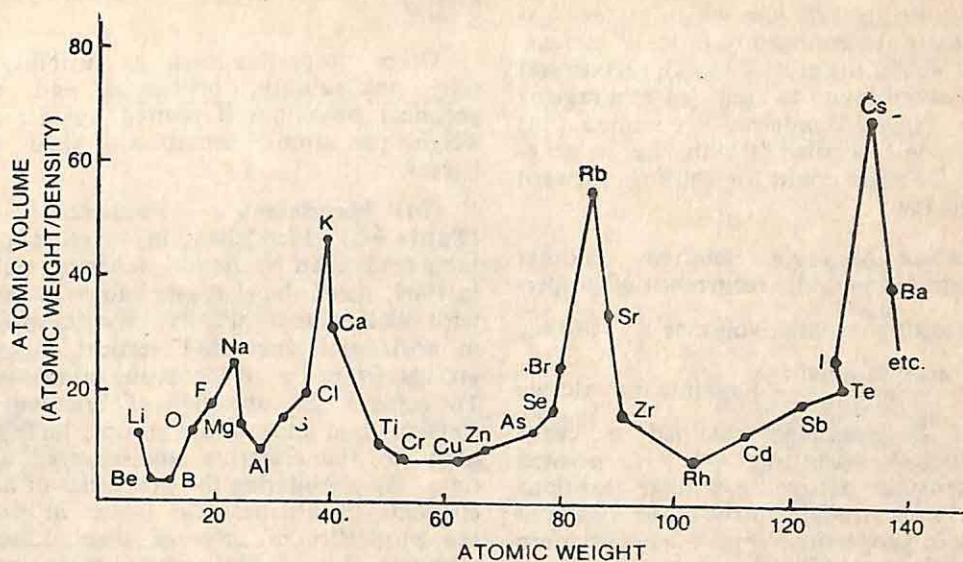


Fig. 4-1. Periodic variation of atomic volume with increasing atomic weight

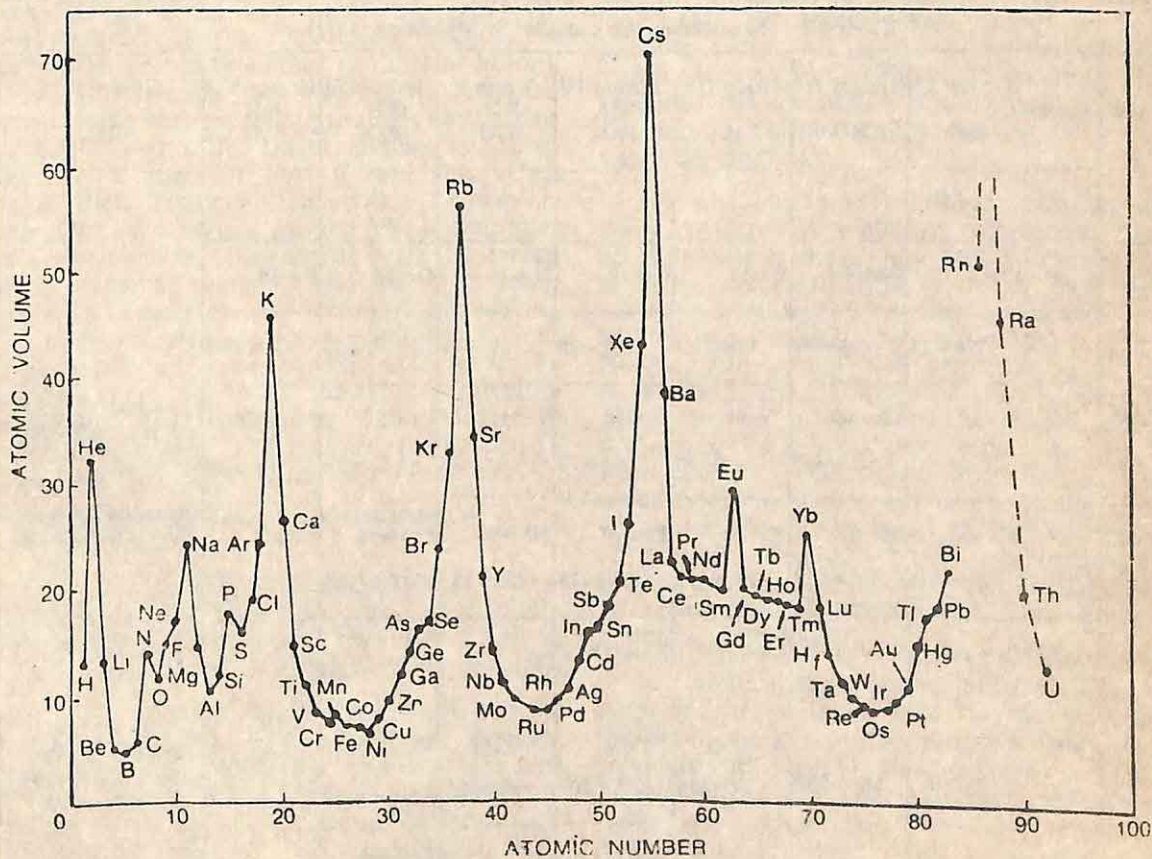


Fig. 4-2. Modern version of Lothar Meyer's curve, i.e., periodic variation of atomic volume with increasing atomic number

their compounds. Their classifications were based upon the *periodic law*, which states that if the elements are arranged in order of increasing atomic weight (or atomic mass), certain sets of properties are found to recur (or at a regular interval). Since Mendeleev presented his arrangement in a detailed fashion, he is generally given the main credit for putting forward the periodic law.

(ii) **Lothar Meyer's Scheme.** Lothar Meyer illustrated periodic recurrence of properties by plotting atomic volumes (atomic

volume = $\frac{\text{atomic weight}}{\text{density}}$) against the atomic weights of elements and obtained a curve similar to one shown in Fig. 4-1. He pointed out that elements occupying similar positions on the peaks and troughs in the curve displayed periodicity in properties. Fig. 4-2 is a modern version of Lothar Meyer's curve based on atomic number. On the basis of his curve, Lothar Meyer included 56 elements in his

periodic table, arranged in groups and sub-groups.

Other properties such as fusibility, volatility, malleability, brittleness and electrochemical behaviour if plotted against atomic weight (or atomic numbers), yield similar curves.

(iii) **Mendeleev's Periodic Table** (Table 4-3) Mendeleev, in his first periodic table (based on Newlands' scheme) published in 1869, listed the elements known at that time with related chemical and physical properties in horizontal rows and vertical columns or groups in order of increasing atomic weights. To achieve the objective of bringing similar elements into appropriate groups, he left some gaps for the elements undiscovered at that time. By considering the properties of adjacent elements in his periodic table, he predicted the properties of some of these undiscovered elements that would occupy these gaps after their discovery. Eventually, when these elements were discovered, it was amazing to

Table 4-3 The periodic table compiled by Mendeleev (1871)

Period	Series	Group I R_1O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_5 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII RO_4
1	1	H=1							
2	2	Li=1	Be=9.4	B=11	C=12	N=14	O=16	F=19	
3	3	Na=23	Mg=24	Al=27.3	Si=28	P=31	S=32	Cl=35.5	
4	4	K=39	Ca=40	?=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56 Co=59 Ni=59 Cu=63
	5	(Cu=63)	Zn=65	?=68	?=72	As=75	Se=78	Br=80	
5	6	Rb=85	Sr=87	Y=88	Zr=90	Nb=94	Mo=96	?=100	Ru=104 Rh=104 Pd=106 Ag=108
	7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
6	8	Cs=133	Ba=137	La=138	?Ce=140	—	—	—	Os=195 Ir=197 Pt=198 Au=199
	9	(—)	—	—	—	—	—	—	
	10	—	—	Er=178	?=180	Ta=182	W=184	—	
	11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
7	12				Tl=231		U=240		

Table 4-4 A comparison of properties predicted by Mendeleev (1871) with those currently accepted for germanium

Property	Predicted	Current
Colour	Dirty grey	Greyish-white
Atomic weight	72	72.6
Density (g/cm ³)	5.5	5.35
Heating in air	EsO ₂	GeO ₂
Properties of oxide :		
physical state	White solid	White solid
density (g/cm ³)	4.7	4.703
Compound formed on chlorination	EsCl ₄	GeCl ₄
Properties of chloride :		
boiling point (°C)	below 100	84
density (g/cm ³)	1.9	1.884
physical state	Colourless liquid	Colourless liquid
Action of acids	Slight	None by HCl or H ₂ SO ₄
Action of alkalis	Pronounced	Dissolved by conc. NaOH
Preparation	EsO ₃ + C → Es + CO ₂	GeO ₂ + C → CO ₂ + Ge

find that they fitted correctly in his table. The element corresponding to the gap between calcium (group II) and titanium (group IV) was named by him as eka-boron (because its properties should be similar to those of boron). The two elements for which gaps remained in the table between zinc (group II) and arsenic (group V) were called eka-aluminium and eka-silicon. During the next fifteen years, when these three predicted elements, known as scandium (eka-boron), gallium (eka-aluminium) and germanium (eka-silicon) were discovered their properties compared very well with those given by Mendeleev. To show the astonishing accuracy of Mendeleev's predictions, let us compare the properties of eka-silicon which he predicted in 1871 with those of germanium discovered in Germany by C.A. Winkler in 1886 (Table 4-4). Mendeleev published an improved periodic table in 1871 (Table 4-3).

Important Features of Mendeleev's Periodic Table

1. The table is divided vertically into 8 columns known as groups and horizontally into rows known as series. (We now call them as periods. These are shown in the Table 4-3).

2. The similarities in the properties of the elements within a group are more marked. Basically in arranging the elements he considered chemical properties, in particular, the ratios in which the elements combine with oxygen or hydrogen. To emphasize this he put the formula of the group oxide and

hydride below the group number in his periodic table.

3. He left some blank spaces in his periodic table. Using the properties of the element located around the blank positions he predicted the properties of some undiscovered elements that would occupy the blank spaces after their discovery.

4. The table was helpful in establishing the valency (group number of elements correspond to their valencies) and atomic masses of elements. Element beryllium for a long time was considered to be an analogue of aluminium and its oxide was assumed to have the formula Be₂O₃. Atomic mass of beryllium was known to be 13.5 on the basis of its properties. Mendeleev had placed it in 2nd group above magnesium. So, its oxide must have the formula BeO. On this basis the atomic weight of beryllium was found to be nine which was confirmed soon after. Its atomic weight was corrected later. Thus by placing the elements strictly according to the similarity in the properties, Mendeleev was able to correct certain atomic masses.

5. Some elements appeared to be out of place in the periodic table on the basis of accepted values for their atomic weights, i.e., elements with higher atomic weights preceded those with lower atomic weights. Mendeleev placed such elements (Te and I; Co and Ni) in locations consistent with their properties, and attributed the apparent reversal of atomic

Table 4-5. A periodic table based on Mendeleev's table of 1871. The circles indicate elements not known in 1871. Table gives the currently accepted values of atomic weights. Numbers in parentheses are the mass numbers of the most stable isotopes.

A ^I B		A ^{II} B		A ^{III} B		A ^{IV} B		A ^V B		A ^{VI} B		A ^{VII} B		A ^{VIII} B		
H 1.0																He 4.0
Li 6.9		Be 9.0			B 10.8		C 12.0		N 14.0		O 16.0		F 19.0			Ne 20.2
Na 23.0		Mg 24.3			Al 27.0		Si 28.1		P 31.0		S 32.1		Cl 35.5			Ar 39.9
K 39.1		Ca 40.1		Sc (45.0)		Ti 47.9		V 50.9		Cr 52.0		Mn 54.9		Fe 55.8	Co 58.9	Ni 58.7
	Cu 63.5		Zn 65.4		Ga 69.7		Ge 72.6		As 74.9		Se 79.0		Br 79.9			Kr 83.8
Rb 85.5		Sr 87.6		Y 88.9		Zr 91.2		Nb 92.9		Mo 95.9		Tc 98.9		Ru 101.1	Rh 102.9	Pd 106.4
	Ag 107.9		Cd 112.4		In 114.8		Sn 118.7		Sb 121.8		Te 127.6		I 126.9			Xe 131.3
Cs 132.9		Ba 137.3		La [*] 138.9		Hf 178.5		Ta 180.9		W 183.9		Re 186.2		Os 190.2	Ir 192.9	Pt 195.1
	Au 197.0		Hg 200.8		Tl 204.4		Pb 207.2		Bi 209.0		Po (210)		At (210)			Rn (222)
Fr (223)		Ra 226.0		Ac ⁴⁴ (227)												

Ce 140.1	Pr 142.9	Nd 144.5	Pm (147)	Sm 150.4	Eu 152.0	Gd 157.3	Tb 158.9	Dy 162.5	Ho 164.9	Er 164.9	Tm 167.3	Yb 173.0	Lu 175.0
Th 232.0	Pa 231.0	U 238.0	Np 237	Pu (242)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (254)	Fm (253)	Md (256)	No (254)	Lr (257)

weights to their incorrect values. Later these values were found to be correct.

The periodic table has been modified, since Mendeleev first formulated it, to give an improved interpretation of the chemistry of the elements. In these improved versions of the table, the basic format has been retained, which is an indication of its acceptability as a basis of discussion of the chemistry of the elements. A periodic table based on Mendeleev's 1871 table is shown in Table 4-5. Each group of the table has been divided into two sub-groups 'A' and 'B'. The resemblances of the properties of the elements within a sub-group are more marked than those between members of the two sub-groups. It includes elements that had not yet been discovered in 1871 (shown in O). In the table, under the head of zero group, inert gases have been placed. These gases could not be foreseen by Mendeleev as he did not leave any space for them. The first inert gas was discovered in 1894 by Lord Rayleigh and Sir William Ramsay.

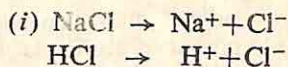
Defects in the Mendeleev's Periodic Table (1871) and its Improved Versions

1. **Anomalous pairs** : Certain elements of higher atomic masses preceded those having lower atomic masses, e.g., Argon (Ar, atomic mass 39.9) is placed before potassium (K, atomic mass 39.1); tellurium (Te, atomic mass 127.6) comes before iodine (I, atomic mass 126.9); cobalt (Co, atomic mass 58.9) is placed before nickel (Ni, atomic mass 58.7).

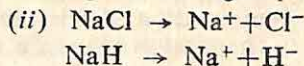
2. **Position of isotopes.** Isotopes were not given separate places even though they had different atomic masses.

3. **Similar elements separated, dissimilar elements grouped together.** Some chemically similar elements were placed in different groups while some other elements which differ sharply from one another in properties were grouped together. For example, highly active metals like sodium and potassium are grouped with copper, silver and gold which are far less active. Barium, lead and mercury have similar properties but these are placed in different groups.

4. **Position of hydrogen.** Hydrogen resembles both alkali metals and halogens in its properties. Hence it claims two positions, that is,



Behaves similar to sodium, thus hydrogen claims its position in group I



Behaves similar to chlorine, thus hydrogen claims its position in group VII

But hydrogen had been assigned place in group I only.

4-3 MODERN BASIS OF CLASSIFICATION

The periodic table has been modified from time to time since Mendeleev first formulated it. Additional elements have been added as they were discovered. The very basis upon which the periodic table was founded has been changed. Mendeleev believed that the periodicity was a function of atomic weight. Now with the determination of atomic numbers by Henry Moseley* (1913), it was realized that the atomic number of an element is a more fundamental feature than its atomic weight and accordingly the periodic law advanced by Mendeleev was changed. Thus today periodicity is based upon atomic number, not atomic weight. Mendeleev could not possibly have reached this conclusion since the electron and proton were not discovered until 1897 and 1902 respectively and atomic numbers were not known until 1913.

The *modern periodic law* proposed by Moseley states that *the properties of the elements are periodic function of their atomic numbers.*

Accordingly, the problem of accommodating the isotopes could be satisfactorily solved by keeping them in one place only (isotopes have the same atomic number). The introduction of atomic number also explained certain difficulties seen in connection with atomic masses in the Mendeleev's table. The anomaly of placing argon before potassium is solved as

Henry Moseley, in 1913, bombarded some metals with high speed electrons in a cathode ray tube. It was observed that X-rays so produced were characteristic for each element. Moseley further observed that the wavelengths of the characteristic peaks in the X-ray spectra were related to the atomic numbers of the elements. He was able to interpret his finding by concluding that the atomic number is a measure of the positive charge in the atomic nucleus. The atomic number then, becomes a much more fundamental quantity than the atomic weight.

the atomic number of argon is 18 and that of potassium is 19. The inversions of iodine and tellurium; and nickel and cobalt could also be thus explained.

It has now been realized that the atomic number dictates the number of electrons in an atom. Electronic structures of the atoms of the elements vary periodically with atomic number. Thus the periodic recurrence of similar electronic configuration leads to a periodic recurrence in chemical properties also.

A more satisfactory statement of the periodic law can thus be arrived as given below :

"Since the electronic structures of atoms of the elements varies periodically with atomic number, all properties dependent on atomic structure also tend to vary periodically with atomic number."

4-4 THE MODERN PERIODIC TABLE—THE LONG FORM

Over the years the periodic table has taken a variety of forms. There has been the short form, the long form, spiral tables, three dimensional helical tables and a number of others. The periodic table the most commonly accepted and used today is a version of the long form. Classification of elements in the long form of periodic table is based on their electronic configurations. The elements are arranged in the increasing order of atomic numbers so that the facts described by the periodic law are efficiently organized. Firstly, all those elements that are most similar get placed in the same vertical column. Secondly, elements get arranged in an orderly manner in periods and present the transition from beginning to end of the period.

Table 4-6 The long form of periodic table

A PERIODIC CLASSIFICATION OF THE ELEMENTS

THE ATOMIC NUMBER IS GIVEN ABOVE THE SYMBOL OF THE ELEMENT

s-BLOCK

IA												p BLOCK						0
I	H											IIA	IIIA	IVA	VA	VIA	VIIA	He
3	4											Li	B	C	N	O	F	Ne
11	12											Be	13	14	15	16	17	18
Na	Mg	d- BLOCK (TRANSITION ELEMENTS)											Al	Si	P	S	Cl	Ar
		IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB									
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	Ba	*SEE BELOW	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
87	88	89-103	104	105	106													
Fr	Ra	SEE **	Ku†	Ha	?													

*LANTHANIDE SERIES

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

**ACTINIDE SERIES

89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	Na	Lr

†OR Rf IN DISPUTE

The periodic table provides a valuable framework for organizing and systematizing the study of elements and their compounds. It has been found that periodic recurrence of similar electron configurations leads to a periodic recurrence of chemical properties. In other words it can be expressed that the chemical as well as physical properties of the elements are related to their electronic structures. It is not possible to explain all the characteristics known of the elements from their electronic configurations. However, from this classification one can correlate many experimentally observed properties with electronic configuration. One can understand the causes of periodicity in properties and general trends in the behaviour of elements. The salient features of the table are illustrated through the Table 4-6. In this table, elements have been divided into four chief blocks, known as *s*-block, *p*-block, *d*-block and *f*-block on the basis of electronic configurations. About this division you will study later in higher classes. The blocks are also named after the general characteristics of the elements. For example, *s*- and *p*-blocks, the main groups consist of the active

metals and non-metals respectively (the *p*-block also contains some metals). The *d*-block is called the 'transition block' since its properties are intermediate—between those of the two main blocks. The *f*-block elements are described as 'inner-transition elements'.

The vertical columns which bring together similar elements are called *groups* or *families*. There are 18 groups. These groups are numbered using Roman numerals (*i.e.*, from I to VIII), zero and letter (A and B), *e.g.* IA, IIB, etc.

Sometimes groups are designated by names: Group IA elements (excluding H) are called the *alkali metals*; Group IIA elements are called the *alkaline earth metals*; the elements of group VIIA are called *halogens*; and those of Group O are the *inert or noble gases* (Fig. 4-3).

The elements of all the A groups, *i.e.*, from IA, IIA...to VIIA and O are collectively called the *representative elements*. The elements in the B groups and those in Group VIII are called *transition elements*. In group IIB, 14

The diagram illustrates the periodic table with various groups highlighted and labeled. The main body of the table is as follows:

ALKALI METALS												NOBLE GASES	
Li	Be											F	He
Na	Mg											Cl	Ne
K	Ca	TRANSITION METALS										Br	Ar
Rb	Sr											Kr	
Cs	Ba											Xe	
Fr	Ra											Rn	
												At	

Below the main table, two additional rows are shown:

LANTHANIDES													
ACTINIDES													

Labels with arrows point to the corresponding groups: ALKALI METALS (Group 1), ALKALINE EARTHS (Group 2), TRANSITION METALS (Groups 3-10), HALOGENS (Group 17), and NOBLE GASES (Group 18).

Fig. 4-3 Different groups of elements

extra elements are placed along with lanthanum and the same number of extra elements are kept with actinium. They are called 'lanthanides' and 'actinides' and are classified separately outside the body of the table. They are called *inner-transition elements*.

The horizontal rows of the table are called *periods*. There are seven periods in all. Each period is numbered by the number of the outermost energy level of the atoms in which the electrons are gradually filled as the atomic number increases. For example, the electronic configuration of chlorine (2, 8, 7) suggests that this is an element from period 3 because the outermost shell is numbered 3 (or M).

Periods are sometimes called short and long periods, depending upon the number of elements.

The first period consists of H and He and is called *very short period*.

The second period consists of eight elements from Li to Ne. In the third period also, there are eight elements from Na to Ar. The second and third periods are called *short periods*.

The fourth and fifth periods have 18 elements each. They are called *long periods*. These periods also include transition elements. The sixth period with 32 elements is called *very long period*. It includes 14 rare earth elements from atomic number 58 to 71 (lanthanides). They all are placed in one box because of similar properties. The 7th period is incomplete having 26 elements and is also called a *very long period*. It includes elements from atomic number 90 to 103 (actinides). Similar to lanthanides, they are also placed in one box.

4-5 PERIODIC PROPERTIES—THE PERIODIC TABLE

It is a matter of general experience that atoms with similar outershell electronic configuration

have similar chemical properties, hence, if one can arrange all known atoms in some systematic fashion according to their electronic structures, periodic recurrence in chemical properties would be evident. For example, both F and Cl with seven electrons in the outermost shell combine with hydrogen and sodium to form similar compounds, i.e., HF(g), HCl(g), NaF(s), NaCl(s).

Many characteristic atomic properties depend upon electronic configuration/atomic number and thus show periodic variation. We will now discuss some of these properties and see how this periodic variation takes place within the periodic table.

Gradation of properties of elements in groups and periods

(i) **Valency.** The electrons occupying the outermost shell are referred to as valence electrons, which in turn determine the valency of an element.

The valency of an element can be inferred from its position in the periodic table. The valency of representative elements is usually given by periodic group number (G) and/or (8-G). For example, elements belonging to groups IA, IIA, IIIA and IVA exhibit valencies 1, 2, 3 and 4 respectively in combination with hydrogen. Elements from groups VA, VIA and VIIA show trivalency, bivalency and monovalency (8-G) respectively in combination with hydrogen and chlorine (Table 4-7). On the other hand elements from group IA to VIIA show valencies 1 to 7 in combination with oxygen (Table 4-8).

Transition elements exhibit variable valency but all of them exhibit a common valency of 2.

In a group all the member elements show the same valency in combining with other elements. For example, the formation of HF

Table 4-7 Valence electrons and valency with respect to hydrogen and chlorine for the first short period elements

Property	Li	Be	B	C	N	O	F
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Valence electrons	1	2	3	4	5	6	7
Valency with respect to hydrogen and chlorine	1	2	3	4	3	2	1
Examples:							
Hydride	LiH	BeH ₂	BH ₃ (B ₂ H ₆)	CH ₄	NH ₃	OH ₂ (H ₂ O)	FH (HF)
Chloride	LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	OCl ₂ (Cl ₂ O)	FCI (ClF)

Table 4-8 Valence electrons and valency with respect to oxygen for the second short period elements

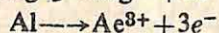
Property	Na	Mg	Al	Si	P	S	Cl
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Valence electrons	1	2	3	4	5	6	7
Valency with respect to oxygen	1	2	3	4	5	6	7
Example :							
Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅ (P ₄ O ₁₀)	SO ₂	Cl ₂ O ₇

Table 4-9 Formulae of compounds of hydrogen with elements of representative groups

Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA
Group valency with hydrogen	1	2	3	4	3	2	1
	LiH	BeH ₂	BH ₃ (B ₂ H ₆)	CH ₄	NH ₃	H ₂ O	HF
	NaH	MgH ₂	AlH ₃	SiH ₄	PH ₃	H ₂ S	HCl
	KH	CaH ₂	GaH ₃	GeH ₄	AsH ₃	H ₂ Se	HBr
	RbH	SrH ₂	InH ₃	SnH ₄	SbH ₃	H ₂ Te	HI
	CsH	BaH ₂	TlH ₃	PbH ₄	BiH ₃		

from fluorine and hydrogen (one fluorine atom combines with one hydrogen atom) enables one to predict that chlorine and other group VIIA elements also form compounds with hydrogen in the atomic ratio of 1 : 1 (HCl, HBr, HI). This relationship is further illustrated in Table 4-9.

(ii) **Metallic and non-metallic nature of the elements.** Metals tend to form positive ions and non-metals tend to form negative ions. From this point of view, metallicity and non-metallicity are entirely relative and are related to electronic structures. If you recall, you will remember that Na, Mg and Al can be converted into positively charged ions, e.g.,



Such elements are called electropositive elements. Now if you refer to the periodic table, you will see that in going from left to right within a period, each successive element has one additional electron added to the same shell and one additional proton added to the nucleus. The result is an increase in electron density. The corresponding nuclear charge exerts a greater attraction for the electrons. As a result of this, valence electrons are pulled more effectively by the nucleus.

Now on comparing the elements from the same period, say sodium and magnesium, it is concluded that valence electron in sodium is less tightly bound than in magnesium. It is, therefore, easier to remove an electron from sodium than from magnesium. On the basis of a similar argument, the elements belonging to the period 3 will lose an electron in the following order : Na > Mg > Al > Si > P > S > Cl. In other words the electropositive or metallic character decreases from Na → Mg → Al → Si → P → S → Cl.

Elements like F, O, N, etc. acquire electrons and become negatively charged ions. Such elements are called electronegative elements. On the basis of logic used earlier there is an overall decrease in the size of an atom across a period from left to right. In general, as the size decreases the atom becomes more compact and the effect of nuclear charge becomes more pronounced. This results into a corresponding increase in the ability of the atom to attract an electron to itself. Thus, F will have a stronger tendency to acquire electron than O and N. Therefore, fluorine is more electronegative than oxygen and nitrogen. Thus in a period electronegative or non-metallic character gradually increases from Li → Be → B → C → N → O → F.

Elements show an increase in electropositive character within a periodic group from top to bottom.

With each successive element, the added electrons occupy new energy levels. Despite the increased nuclear charge this causes an increase in distance of the electrons present in the outermost shell from the nucleus. Thus the addition of a new energy level to an atom dominates over the effect of increase in the nuclear charge. As a result of this, electrons present at a larger distance can be removed easily as compared to the electrons close to the nucleus. This ease of removal of electrons from an element makes it more electropositive. Thus, for group IA elements the ease of removal of an electron increases from $\text{Li} \rightarrow \text{Na} \rightarrow \text{K} \rightarrow \text{Rb} \rightarrow \text{Cs}$, i.e., the electropositive character increases from lithium to caesium. On the basis of this logic one can also explain the transition from non-metallic to metallic nature observed in group IVA, VA and VIA elements. In group IVA, C is a non-metal but Sn and Pb are metals. Similarly in group VA, N is a non-metal whereas Bi is a metal. In group VIA, oxygen and sulphur are non-metals whereas Te is a metalloid. Fig 4-4 shows the progressions of all the periodic properties just discussed.

Further support to the trends observed in the case of metallic and non-metallic nature of elements can be arrived by knowing the nature of oxides. Trends in the acid-base character of the oxides of *s*- and *p*-block elements (representative elements) are shown in Fig. 4-5. Electropositive elements form basic oxides whereas the electronegative elements form acidic oxides.

(iii) **Atomic radius (size) of atoms and ions.** Atoms and ions possess no finite size owing to uncertainty in the position of orbiting electrons around the nucleus. However, the size of an atom can be estimated from its atomic radius which is defined as the most probable distance from the nucleus to a point where the electron density is effectively zero (negligible). To measure the atomic radius the distance between the nuclei of two adjacent atoms in a molecule is determined spectroscopically. One half of internuclear distance gives the atomic radius for a homonuclear diatomic molecule.

Ionic radius is defined in a similar manner, being half the distance between the nuclei of two nearest neighbours in a close packed lattice. Ionic radius may be either bigger or smaller than atomic radius depending upon the nature of the ion formed from the neutral atom. The cation formed by the loss of electrons, is smaller than the parent atom, i.e.,

Element	Atomic radius	Ionic radius
Sodium (Na)	$\text{Na} = 1.57 \text{ \AA}$	$\text{Na}^+ = 0.98 \text{ \AA}$

On the other hand, the anion, formed by the addition of electrons, is bigger than the parent atom, i.e.,

Element	Atomic radius	Ionic radius
Chlorine (Cl)	$\text{Cl} = 0.99 \text{ \AA}$	$\text{Cl}^- = 1.81 \text{ \AA}$

Multiplicity of the bond and the nature of bond also affect the radii of atoms in compounds.

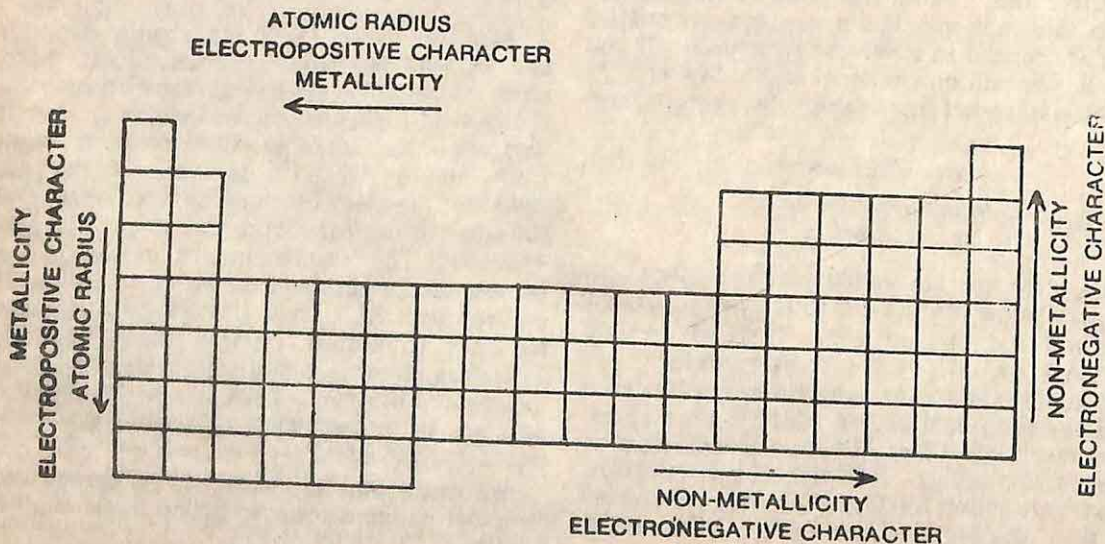


Fig. 4-4. Some periodic trends increasing in the direction of arrows

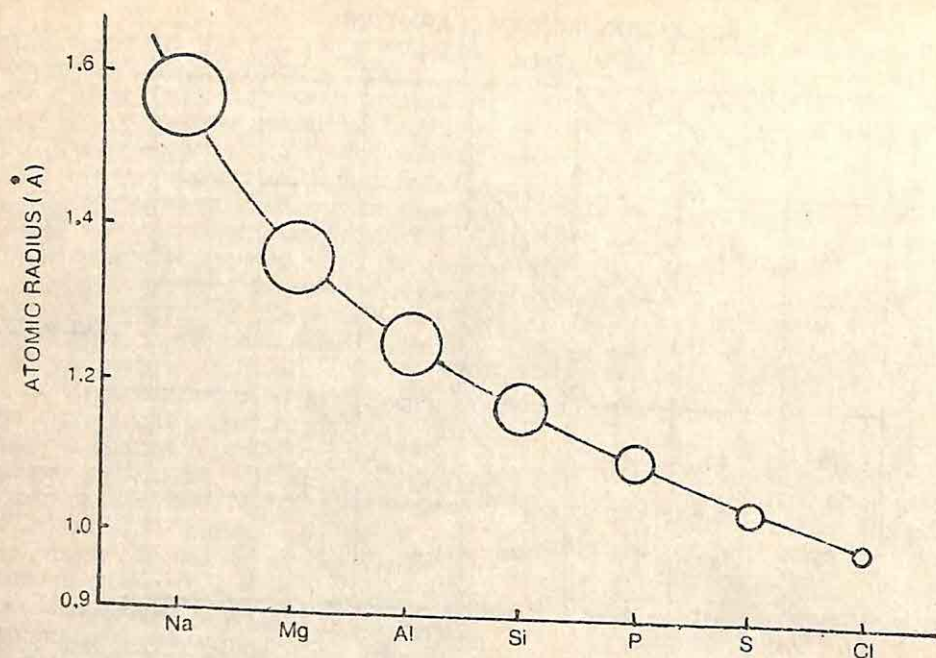


Fig. 4-7 Trends in atomic radii of 3rd period elements (atomic radius decreases from Na to Cl)

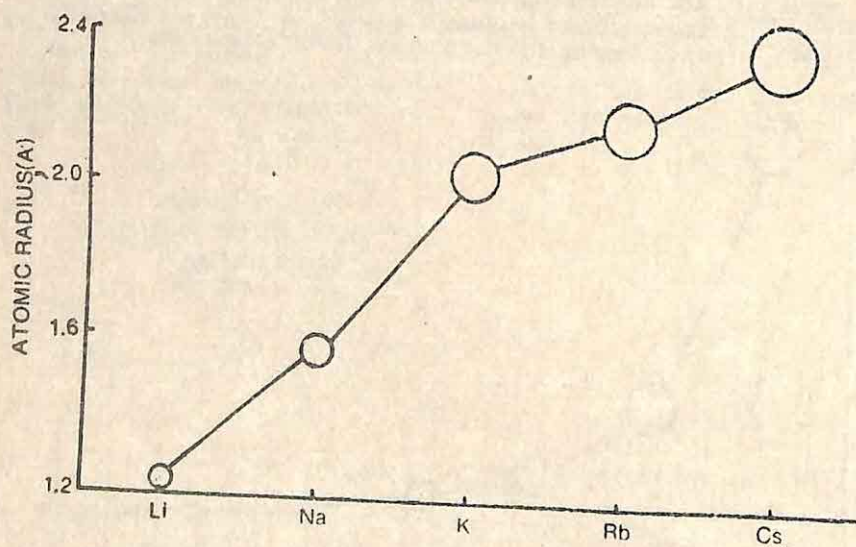


Fig. 4-8 Trends in atomic radii of alkali metals (atomic radius increases from Li to Cs)

In general, the size of the atom gradually decreases as we proceed from left to right across a period in the periodic table. (Figs. 4-4, 4-6 and 4-7).

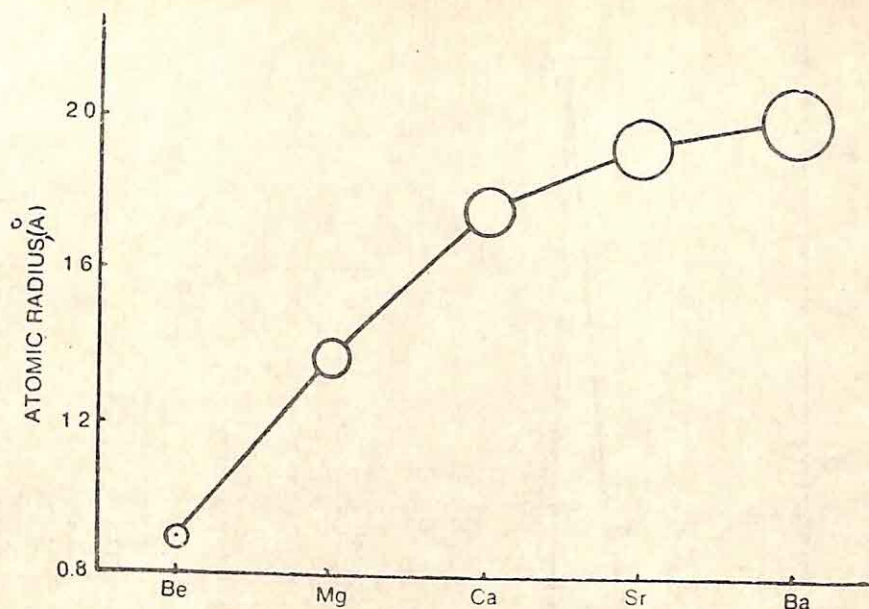


Fig. 4-9 Trends in atomic radii of alkaline earth metals (Atomic radius increases from Be to Ba)

This is because of the increasing nuclear charge while the electrons are added to the same shell. Due to an increase in the nuclear charge, the electrons are attracted toward the nucleus to a great extent and thus atomic radius decreases. But the inert gases at the end of periods do not follow suit because of their complete valence shells. Electrons within the valence shell repel one another. As a result of this, the electron cloud expands and thus size increases. (Table 4-10 on page 81).

On the other hand the size of the atom generally increases as we move down within a group (Figs. 4-4, 4-8 and 4-9 ; Tables 4-11 and 4-12). This trend is expected as it corresponds to the addition of electrons in successive energy levels. Although the nuclear charge increases, the net effect of additional new energy shell is very large and outweighs the contractive effect of the increased nuclear charge.

(iv) **Density, melting point and boiling point.** Elements show periodic variation for these properties also. For example, if we consider the periods of representative elements, we observe that densities, (Table 4-10) melting and boiling points (Table 4-10) of elements increase across the period and reaches a maximum value in the middle of the series. It can be realized from Fig. 4-10 that carbon (in the middle of second period) and silicon (in the middle of third period) have the highest melting points in period 2 and 3 respectively. Similarly transition elements also attain the highest values for these properties in the middle of the series.

A general gradation in these properties is also observed in a periodic group. Generally densities increase while melting and boiling points decrease in moving down the group. (Tables 4-11 and 4-12 ; Figs. 4-11, 4-12, 4-13 and 4-14 on page 81 & 82).

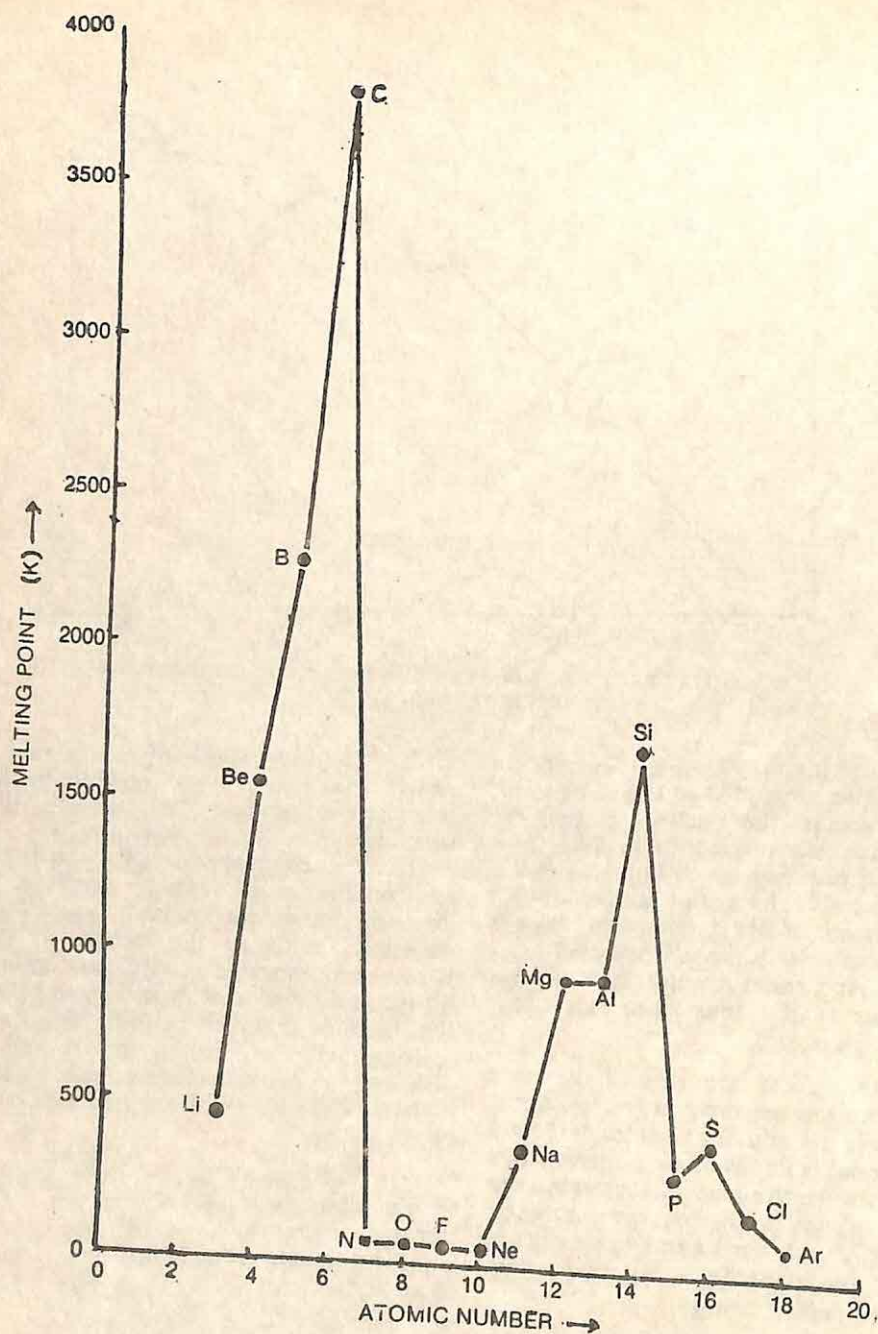


Fig. 4-10 Melting points of the elements versus their atomic numbers

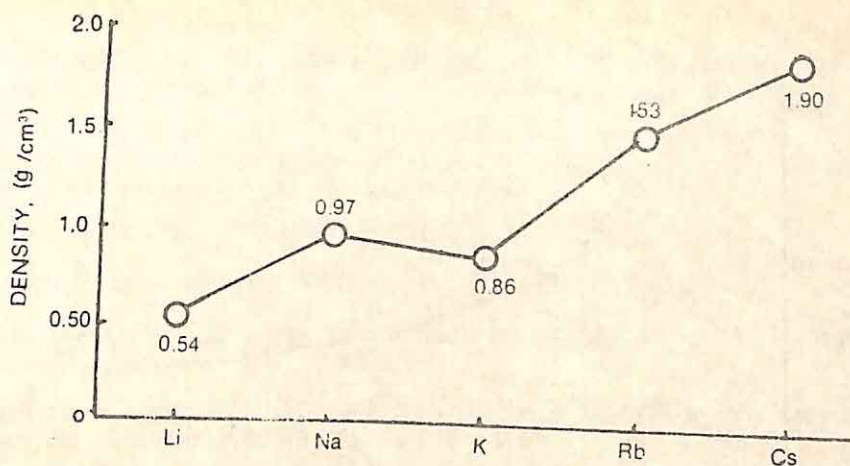


Fig. 4-11 Trends in densities of alkali metals

Table 4-10 Densities, atomic sizes, melting and boiling points of the second and third period elements

Elements of second period	Li	Be	B	C	N	O	F	Ne
Density, g/cm ³	0.54	1.86	2.34	3.51 (diamond) 2.22 (graphite)	0.87	1.14	1.11	—
Atomic size, Å	1.23	0.89	0.8	0.77	0.75	0.74	0.72	1.54
Melting point, K	454	1550	2273	3800	63.2	54.6	53	24.4
Boiling point, K	1620	2733	2823	4473	77.2	90	85	27.2
Elements of third period	Na	Mg	Al	Si	P	S	Cl	Ar
Density, g/cm ³	0.97	1.75	2.70	2.33	1.82 (white)	2.7 (rhombic)	1.50	—
Atomic size, Å	1.57	1.36	1.25	1.17	1.10	1.04	0.99	1.04
Melting point, K	371	924	933	1683	313	392	172	84
Boiling point, K	1165	1380	2740	2628	553	718	238.4	87

Table 4-11 Physical properties of alkali metals

Alkali metal	Atomic number	Atomic radius, Å	Density g/cm ³	Melting point, K	Boiling point, K
Li	3	1.23	0.54	454	1620
Na	11	1.57	0.97	371	1165
K	19	2.03	0.86	336	1047
Rb	37	2.16	1.53	312	961
Cs	55	2.35	1.87	302	951

Table 4-12 Physical properties of halogens

Halogen	Atomic number	Atomic radius, Å	Density g/cm ³	Melting point, K	Boiling point, K
F	9	0.72	1.1	53	85
Cl	17	0.99	1.5	172	238
Br	35	1.14	3.2	266	332
I	53	1.33	4.9	386	456

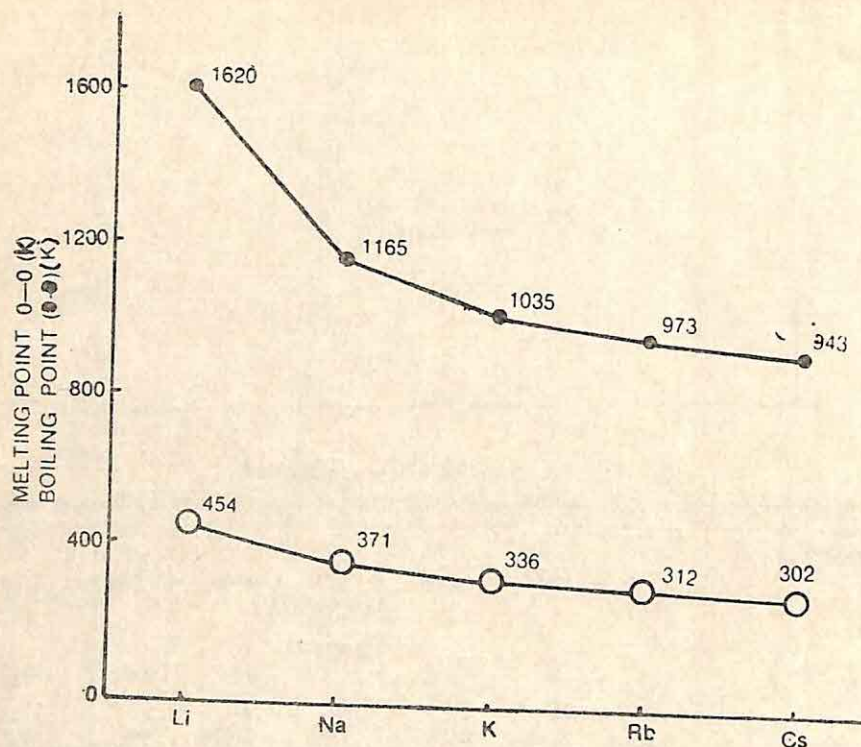


Fig. 4-12 Trends in melting and boiling points of alkali metals

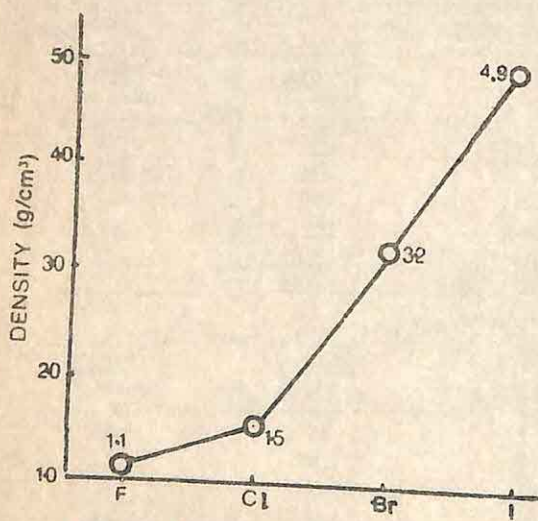


Fig 4-13 Trends in densities of halogens

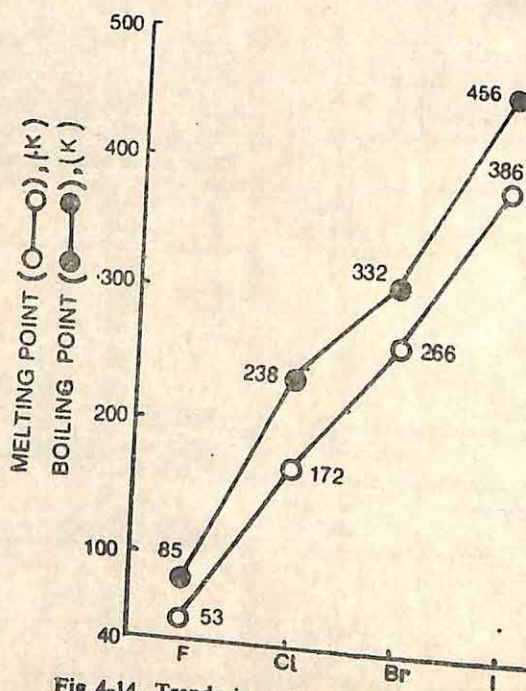


Fig 4-14 Trends in melting and boiling points of halogens

KEY TERMS

- 4-1 **Periodic table** : It is a tabular arrangement of elements on the basis of similarities in properties and electronic configurations into groups and periods.
- 4-2 **Periodic law** : The properties of the elements are periodic function of their atomic numbers. On arranging the elements in increasing order of atomic number, their properties recur at regular intervals.
- 4-3 **Group** : A vertical column in the periodic table is called a group.
- 4-4 **Period** : A horizontal row in the periodic table is called a period.
- 4-5 **Alkali metals** : The group of elements designated as IA in the modern periodic table, e.g., Li, Na, K, Rb and Cs.
- 4-6 **Alkaline earth metals** : The group of elements designated as IIA in the modern periodic table, e.g., Be, Mg, Ca, Sr and Ba.
- 4-7 **Noble gases** : The members of zero group in the modern periodic table, e.g., He, Ne, Ar, Kr, Xe and Rn. They have eight electrons in the outermost shell except helium which has only two electrons.
- 4-8 **Halogens** : The group of elements designated as VIIA in the modern periodic table, e.g., F, Cl, Br and I. They are non-metals and have seven electrons in the outermost shell.
- 4-9 **Representative elements** : The elements of groups IA to VIIA in the long form of periodic table. Their properties adhere closely to the regular progression on which the periodic table is based.
- 4-10 **Transition elements** : The elements of groups IB to VIIB and VIII in the long form of periodic table. Their properties do not follow the regular progression of the periodic table. Elements of group IIB, i.e., Zn, Cd and Hg are not true transition elements.
- 4-11 **Lanthanides** : The 14 elements (from atomic number 58 to 71) immediately following lanthanum in the modern periodic table. Their properties are quite alike and are placed in one box only.
- 4-12 **Actinides** : The 14 elements (from atomic number 90 to 103) following actinium in the modern periodic table. Their properties are quite similar and are placed in one box only.
- 4-13 **Triads** : It is a group of three elements with similar chemical properties. Dobereiner classified some elements in triads.
- 4-14 **Law of octaves** : When the elements are arranged in increasing order of atomic weight, the properties of every eighth element are similar to that of the first element. This law was given by Newlands.
- 4-15 **Metals (or electropositive elements)** : Elements that tend to form positive ions. They are good conductors of electricity. They form basic oxides.
- 4-16 **Non-metals (or electronegative elements)** : Elements that tend to form negative ions. They are poor conductors of electricity. They form acidic oxides.
- 4-17 **Metalloids** : The name sometimes given to elements that have the intermediate properties between those of metals and non-metals. They form amphoteric oxides.

4-18 Atomic volume : The volume occupied by one gram atom of an element in the solid state. It is calculated by dividing atomic weight of an element by density of that element.

4-19 Atomic radius : It is the distance from the nucleus to a point where the electron density is effectively zero. One half of the internuclear distance gives the atomic radius for a homonuclear diatomic molecule.

UNIT THROUGH EXERCISES

4-1. Point out the correct statements of the following :

- (i) The elements, when arranged in order of increasing atomic number, exhibit a periodicity in properties.
- (ii) The size of atoms increases in descending a group in the periodic table.
- (iii) The elements are arranged in the periodic table (long form) in order of their increasing atomic masses.
- (iv) From left to right within a period, the strength with which the nucleus attracts the electrons in the outer energy level increases.
- (v) The elements occupying the centre and left of the periodic table are classified as metals.
- (vi) Mendeleev in his periodic table put argon before potassium even though the atomic weight of argon is higher than that of potassium.
- (vii) Elements having the same atomic masses are called isotopes.
- (viii) Isotopes of elements have been assigned separate place in the long form of periodic table.
- (ix) Magnesium is more electropositive than sodium.
- (x) Elements with 8 electrons in the outer shell are called noble gases.

Ans. Statements (i), (ii), (iv), (v), (vi) and (x) are correct.

4-2. Give the terms used to express the following :

- (a) Vertical columns in a periodic table
- (b) Horizontal rows in a periodic table
- (c) Elements having the same atomic number

(d) Elements which form both acidic and basic oxides

(e) Element having one electron in the outer shell

(f) Elements toward the upper right of the periodic table

Ans. (a) group, (b) period, (c) isotopes, (d) metalloids, (e) alkali metals, and (f) non-metals.

4-3. (a) Using the modern periodic table give the two pairs of elements where the atomic masses are in the opposite order to the atomic numbers.

(b) Which has the larger radius ?

(i) Mg or Ca (ii) S or Cl

(c) Which is more metallic ?

(i) Na or Mg (ii) C or Si

Ans. (a) Argon and potassium ; cobalt and nickel.

(b) (i) Ca (ii) S (c) (i) Na (ii) Si.

4-4. (a) Choose the alkali metal, noble gas, alkaline earth metal, halogen or transition metal of the following elements :

Sr, K, Xe, Zn, Mn, Fe, He, H, F, I, S and C.

(b) What is the fundamental difference between the group A and B elements ?

Ans. (a) Alkali metal : K,
Alkaline earth metal : Sr

Noble gas : Xe, He

Transition elements : Mn, Zn, Fe,

Halogen : F, I,

(b) Group A elements are representative elements and group B elements are transition elements ?

4-5. (a) In terms of electronic configuration, what the elements of a given period and group have in common ?

(b) Which two elements of the following belong to the same period ?

Al, Si, Be and O

- (c) Which two elements of the following have structural similarity ?

Na, K, Ne and Ca

- (d) Which of the following electronic arrangements represent metals ?

2, 8, 8, 2 ; 2, 8, 7 ; 2, 8, 8 and 2, 8, 1

Ans. (a) For elements in a period the number of shells is equal ; for elements in a group the number of electrons in the outermost shell is the same

(b) Al and Si, (c) Na and K

(d) 2, 8, 1 and 2, 8, 8, 2.

5-6 Multiple Choice Questions

4-6. Put a (✓) mark against the most appropriate choice :

- (i) The law of octaves was advanced by
(a) Newlands (b) Dobereiner
(c) Lothar Meyer (d) Mendeleev
- (ii) The basis on which Mendeleev constructed his periodic table is :
(a) atomic number (b) atomic weight
(c) atomic volume (d) atomic size
- (iii) Which of the following elements did not find place in the Mendeleev's original periodic table ?
(a) Aluminium (b) Silicon
(c) Zinc (d) Germanium
- (iv) Which of the following sets of elements do not belong to the same period of the periodic table ?
(a) F, Cl, Br, (b) C, N, O
(c) Na, Mg, Al (d) P, S, Cl
- (v) Which of the following sets of elements do not belong to the same group of the periodic table ?
(a) Cu, Ag, Au (b) Li, Na, K
(c) Mg, Ca, Sr (d) Al, Si, P
- (vi) Which of the following elements is the most electronegative ?
(a) Fluorine (b) Chlorine
(c) Bromine (d) Iodine

- (vii) Which of the following describe the process of addition of an electron to an atom ?

(a) Electronic configuration

(b) Atomic size

(c) Atomic number (d) Valency

- (viii) Which of the following statements concerning atomic size is correct ?

(a) Atomic size increases with increase of atomic number in a period.

(b) Atomic size increases with increase of atomic number in a group.

(c) Atomic size is independent of atomic number.

(d) All of the above.

Ans. (i) (a), (ii) (b), (iii) (d), (iv) (a)
(v) (d), (vi) (a), (vii) (a), (viii) (b)

4-7. Fill in the blanks

- (i) The elements are arranged in the periodic table in order of their increasing
- (ii) The horizontal rows of elements in the periodic table are called
- (iii) The elements in the vertical columns of periodic table constitute
- (iv) The properties of an element are a periodic function of its
- (v) Elements with eight electrons in their outermost energy level are called
- (vi) The elements can be divided into blocks according to their
- (vii) The metallic character with increase of atomic number in a group.
- (viii) From left to right within a period, the strength with which the nucleus attracts the electrons in the outer energy level

Ans. (i) atomic number, (ii) periods, (iii) groups, (iv) atomic number, (v) noble gases, (vi) four, electronic configuration, (vii) increases, (viii) increases.

4-8 Match the descriptions under column B against the statements/terms given under column A.

Column A

Column B

- (i) Periods
- (ii) Groups
- (iii) Copper
- (iv) Aluminium
- (v) Alkali metals
- (vi) Transition elements

- (i) belongs to *p*-block
- (ii) vertical columns of the periodic table
- (iii) belongs to *d*-block elements
- (iv) horizontal rows of the periodic table
- (v) elements belonging to group IA
- (vi) elements from groups IB to VIIB and VIII

REVIEW QUESTIONS

- 4-1 Which of the alkali metals has
- (a) the largest atomic radius.
 - (b) smallest number of electrons per atom.
 - (c) smallest positive ion ?
- 4-2 Predict which ion in each pair is the larger :
- (a) Mg^{2+} or Ca^{2+} , (b) K^+ or Ca^{2+} ,
 - (c) Cl^- or K^+ , (d) F^- or Cl^- ,
 - (e) Na or Na^+ , (f) Br or Br^-
- 4-3 Describe the early attempts to classify the elements leading to Mendeleev's periodic table.
- 4-4 What was the basis on which Mendeleev constructed his periodic table ? What were the essential features of Mendeleev's periodic table ?
- 4-5 State the present day version of the periodic table. How does it differ from that of Mendeleev's ?
- 4-6 Write notes on the following :
- (a) Dobereiner's triads
 - (b) Newlands' octaves
 - (c) Lothar Meyer's curves
- 4-7 What significance does the periodic table have with regard to the development of theory about the electronic structure of the atom ?
- 4-8 Discuss the trends in atomic sizes of elements in the periodic table.
- 4-9 Name the four blocks of elements in the periodic table. State their characteristics.
- 4-10 (a) Which of the following elements belong to *p*-block ?
Na, Al, S, Cl, Cu, Mg, C
- (b) Which elements constitute the halogens, the noble gases and the alkaline earth metals ?

UNIT 5

Chemical Reactions—How Fast and How Far



Michael Faraday
(1791-1861)

Michael Faraday, an English chemist, investigated the masses of substances produced by varying quantities of electricity during the electrolysis of solutions. He invented both electric motor and electric generator.

Learning Objectives

At the completion of this unit, you should be able to:

1. Define a chemical reaction.
2. Classify chemical reactions as decomposition, combination, single displacement or double displacement reactions.
3. Define redox reaction with examples.
4. Define oxidation, reduction, oxidizing agents and reducing agents.
5. Identify the specific elements involved in oxidation-reduction.
6. Illustrate the exothermic and endothermic reactions with examples.
7. Describe the phenomenon of electrolysis.
8. Define anode and cathode in terms of oxidation and reduction.
9. Describe the use of electrolysis in electrorefining and electroplating.
10. Explain the concept of rate of chemical reaction.
11. List four factors that may affect the rate of chemical reactions.
12. Define equilibrium in terms of a reversible reaction.
13. State LeChatelier's principle.
14. Predict changes in equilibrium systems due to change in concentration, pressure and temperature.
15. Describe the relative strength of acids and bases in terms of their ionizations.
16. Calculate hydrogen ion concentrations and pH values of acids and bases.

5-1 INTRODUCTION

We observe various changes around us. Combustion of fuel (domestic fuel gas, wood, coal, etc.) cooking of food, conversion of milk into curd, ripening of fruits, rusting of iron, dissolution of sugar and salt in water, conversion of ice into water, evaporation of water, etc., are some of the common changes which we come across. Some of these are temporary changes and others are permanent changes. Temporary changes are called *physical changes* while permanent changes are called *chemical changes*.

The chemical changes are called *chemical reactions*. A chemical reaction transforms one or more substances into a different set of substances. Combination of hydrogen and oxygen to produce water, burning of magnesium in oxygen to form magnesium oxide, rusting of iron and reaction between nitrogen and hydrogen to form ammonia are chemical reactions. The substances that are consumed in the reaction are called *reactants* and those that are formed during the course of reaction are called *products*. Since millions of reactions are known, it is necessary to classify them in one way or the other. The mode in which reactants react in chemical reactions forms the basis of classification of chemical reactions into various categories.

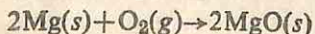
The present unit deals with types of chemical reactions, electron transfer concept of oxidation-reduction reactions, phenomenon of electrolysis and its applications, the rates of chemical reactions and the factors affecting rates and equilibrium in chemical reactions.

TYPES OF REACTIONS AND ELECTROLYSIS

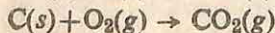
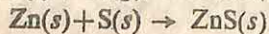
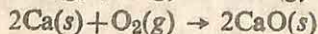
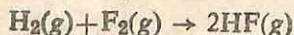
5-2 TYPES OF REACTIONS

5-2-1 COMBINATION REACTIONS

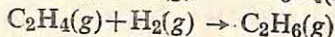
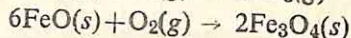
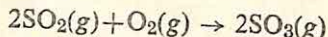
Reactions in which two or more reactants combine to form one product are called combination reactions. For example, formation of magnesium oxide from magnesium and oxygen is a combination reaction.



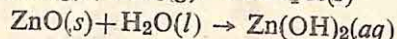
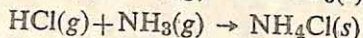
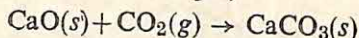
Here two elements combine to form a compound. Other examples are:



There are reactions in which a compound and an element combine and form a new compound. For example,



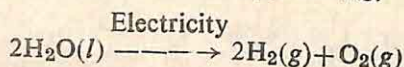
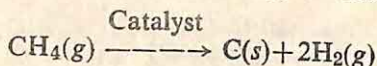
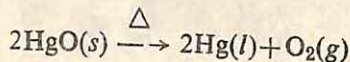
Two compounds can combine and form a new compound. For example,



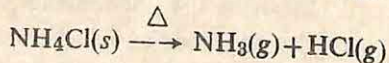
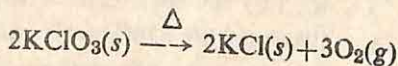
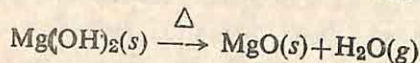
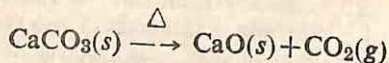
5-2-2 DECOMPOSITION REACTIONS

In decomposition reactions, a compound decomposes into simpler substances. Heat, light, electricity or catalyst is generally used to affect these decomposition reactions. For example,

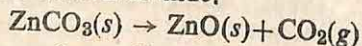
Compounds of two elements will decompose to form the two elements.



A compound may decompose into another compound plus a third compound or an element.



Experiment 5-1. To demonstrate a decomposition reaction. Take about 2.0 g of zinc carbonate in a test tube. Fit the test tube with a cork and a delivery tube bent at an angle as shown in Fig. 5-1. Heat the test tube. Zinc carbonate decomposes producing zinc oxide and carbon dioxide.



Pass carbon dioxide gas through lime water for some time. Observe the change. Lime water turns milky. This is due to the formation of insoluble calcium carbonate.

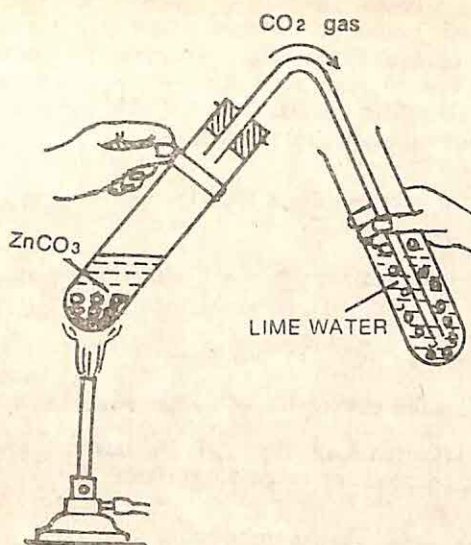
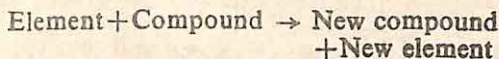


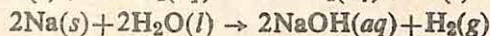
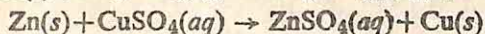
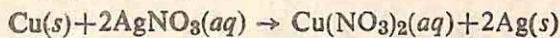
Fig. 5-1. Decomposition of zinc carbonate

5-2-3 SINGLE DISPLACEMENT REACTIONS

In single displacement reactions, an element reacts with a compound to displace one of the elements in the compound.



For example,



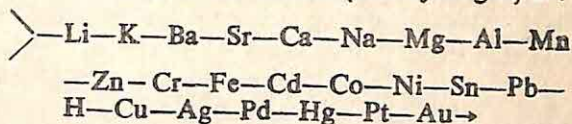
In these reactions, the element displaces another element from a compound because it is more active than the element already present. The activity of the metallic elements increases downward in a periodic group and from right to left in a period in the periodic table. About relative activity of metals you will learn in detail in your higher classes.

There is another type of single displacement reaction in which a salt and a more active non-metal on reacting form a new compound and a less active non-metal.

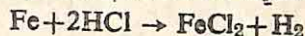


The activity of the non-metallic elements increases upwards in a periodic group and from left to right in a period in the periodic table.

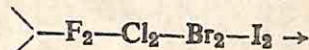
It is possible to predict which elements can replace others in a compound. To make this prediction, we use a list of elements called an *activity series*. An element can replace any element that appears after it in this series. The activity series of the metals (and hydrogen) is :



In the activity series, hydrogen appears after iron, hence, it can be replaced by iron :

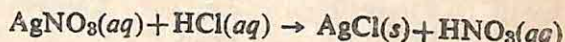


The halogens also have an activity series :

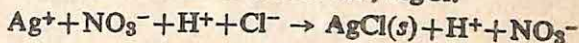


5-2-4 DOUBLE DISPLACEMENT OR DOUBLE DECOMPOSITION REACTIONS

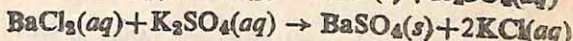
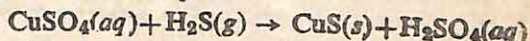
In double displacement reactions, two compounds react to form two new compounds. The positive ion of one compound combines with the negative ion of the other and vice versa. For example,



In this, reaction, Ag^+ ion from AgNO_3 solution combines with Cl^- ion from HCl solution to form insoluble salt, AgCl .



Some more examples are :



The reaction between an acid and a base to form a salt is also considered a double displacement reaction. For example,

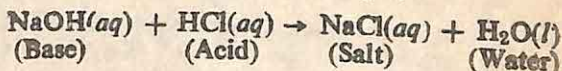


Table 5-1 summarizes the four major types of reactions just discussed. The letters A, B, C and D are general symbols for the elements involved.

Table 5-1 Summary of reactions

Type	Reaction
Combination	$A + B \rightarrow AB$
Decomposition	$AB \rightarrow A + B$
Single displacement	$AB + C \rightarrow AC + B$
Double displacement	$AB + CD \rightarrow AD + CB$

5-2-5 REDOX REACTIONS

Consider a reaction between zinc and copper (II) sulphate in aqueous solution. When a small piece of zinc is placed in a test tube containing blue solution of copper (II) sulphate, zinc gradually disappears and the solution turns colourless (Fig. 5-2).

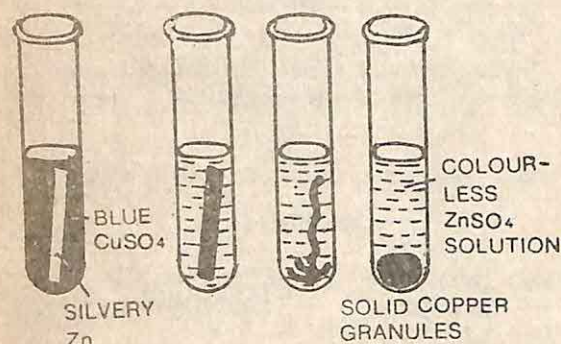
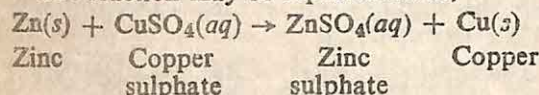
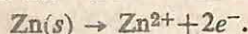


Fig. 5-2 The oxidation-reduction reaction between zinc and copper (II) sulphate

The reaction may be represented as,

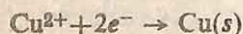


In the above equation, zinc is more electro-positive than copper, hence Zn will pass into solution as Zn^{2+} ions. This is represented as,



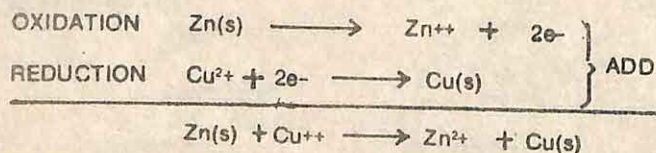
Zinc loses two electrons. This process which involves the loss of electrons is referred to as *oxidation half reaction*.

Cu^{2+} ion from copper sulphate solution will be changed into metallic copper. This is represented as,

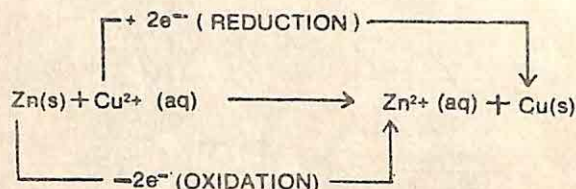


Copper ion gains two electrons. The process which involves gain of electrons is referred to as *reduction half reaction*.

When the two half reactions (oxidation and reduction half reactions) are added, the net equation obtained is,

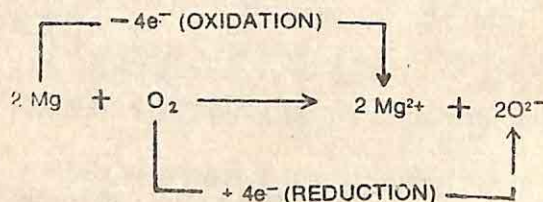


This overall reaction in which both oxidation and reduction occur simultaneously is called oxidation-reduction reaction or more briefly '*redox*' reaction. Zinc loses electrons and is therefore oxidized and Cu^{2+} ion gains electrons and is therefore reduced.



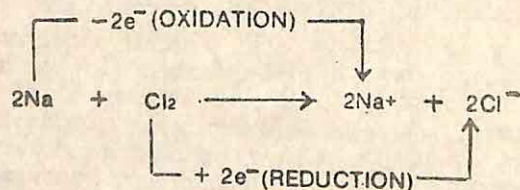
Some more examples of redox reactions

1. The reaction between magnesium and oxygen to produce magnesium oxide,



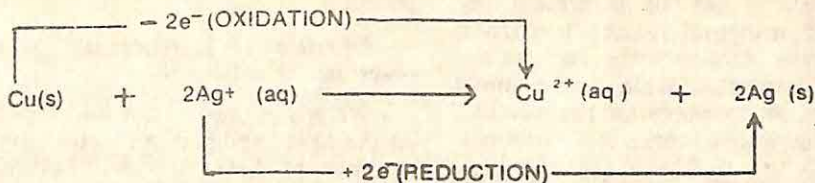
Here magnesium is oxidized and oxygen is reduced.

2. The combination of sodium and chlorine to form sodium chloride.



Here sodium is oxidized and chlorine is reduced.

3. The displacement of silver from silver nitrate by adding copper,



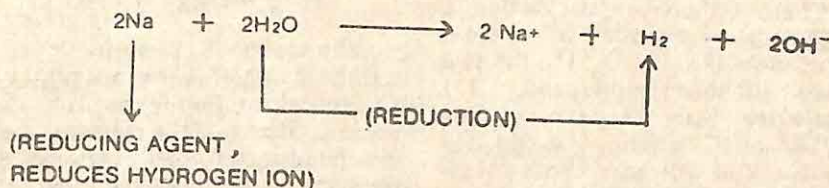
Here copper is oxidized and silver ion is reduced.

Oxidizing and Reducing agents

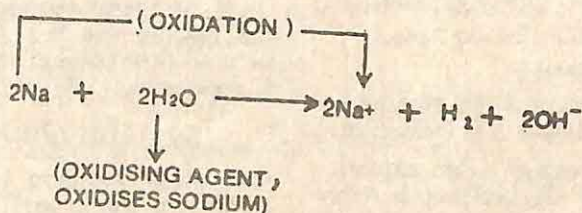
In a redox reaction, one substance acts as an electron donor. It loses electrons and is oxidized. It causes another substance to be reduced. An electron donor that causes another substance to be reduced is called a *reducing*

agent. The substance that gains electrons in a redox reaction is an electron acceptor. By accepting electrons, it is reduced. The electron acceptor causes another substance to be oxidized and is called *oxidizing agent*. For example,

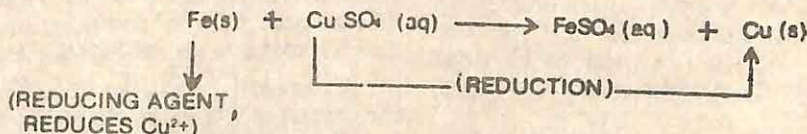
1. Sodium acts as reducing agent,



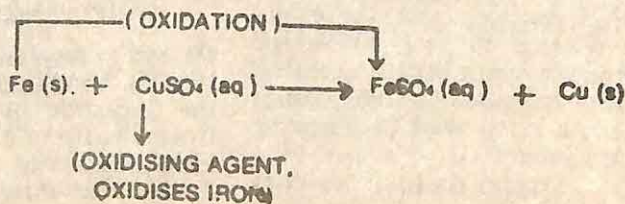
2. Hydrogen ion acts as oxidizing agent,



3. Iron acts as reducing agent,



4. Copper ion acts as oxidizing agent,



In any redox reaction, the substance being oxidized and reduced can be determined by the increase and decrease in the oxidation number. *Oxidation number* may be defined as the charge (or oxidation state) an element appears to have when electrons are counted according to two arbitrary rules:

(a) In a homonuclear molecule, electrons are shared equally between the two atoms, e.g., in a chlorine molecule, the shared pair of electron ($\text{Cl}:\text{Cl}$) is assigned equally to both the atoms and hence the oxidation number of chlorine atom is zero.

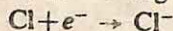
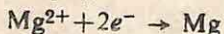
(b) Electrons shared between atoms of two different elements are assigned to the more electronegative element. For example, in hydrochloric acid ($\text{H}:\text{Cl}$), Cl is more electronegative than H; the shared pair of electrons shifts towards Cl atom, therefore, the oxidation number of Cl atom is -1 and that of H atom is $+1$. In water molecule ($\text{H}:\text{O}:\text{H}$), the two pairs of electrons shift towards O atom (O is more electronegative than H atom). The oxidation number of O atom is -2 and that of H atom is $+1$. You will learn about oxidation number in detail in higher classes.

We can now define oxidation and reduction in terms of oxidation number. A process that increases the oxidation number of an element algebraically is oxidation. For example,



In this the oxidation number of sodium has increased from 0 to $+1$ hence it is oxidation.

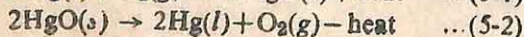
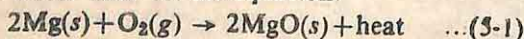
A process that decreases the oxidation number of an element algebraically is reduction. For example,



Here the oxidation number of Mg has decreased from $+2$ to 0 and that of Cl atom from 0 to -1 . Hence these are reduction processes.

5-2-6 EXOTHERMIC REACTIONS AND ENDOTHERMIC REACTIONS

A reaction which proceeds with the evolution of heat is referred to as an *exothermic reaction* and the one in which heat is absorbed is called *endothermic reaction*. The heat change in a chemical reaction is indicated by including the word 'heat' in the equation.



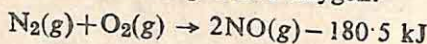
Equation (5-1) represents an exothermic reaction.

Equation (5-2) represents an endothermic reaction.

We are interested not only in the direction of the heat change in a reaction but also in the amount of heat absorbed or evolved. The amount of heat change varies widely from one reaction to another. When one mole of nitrogen combines with 3 moles of hydrogen to form 2 moles of ammonia, 92 kJ of heat is evolved. This may be expressed by writing,

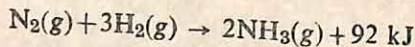


Similarly, we can explain the formation of nitrogen oxide, NO which is an endothermic reaction between nitrogen and oxygen.



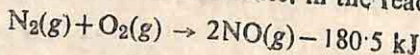
The atoms in a molecule or a compound are held together by chemical bonds. When a chemical reaction takes place, chemical bonds between atoms of the reactant are broken and new bonds are formed between atoms of the products formed. In the bond breaking energy is required and in the bond formation energy is released.

If the energy required in bond breaking of the reactants is less than the energy released in bond formation of the products, the reaction is exothermic. For example, in the reaction,



the energy required to break three ($\text{H}-\text{H}$) bonds and one ($\text{N}\equiv\text{N}$) bond is less than energy released in the formation of three ($\text{N}-\text{H}$) covalent bonds in NH_3 (for two molecules of NH_3) by an amount of 92 kJ. Hence, formation of ammonia by the combination of nitrogen and hydrogen is an exothermic reaction.

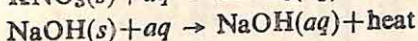
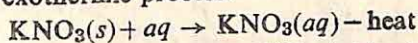
If the energy required in bond breaking of the reactants is greater than the energy released in bond formation of the products, the reaction is endothermic. For example, in the reaction,



the energy required to break ($\text{N}\equiv\text{N}$) bond and ($\text{O}=\text{O}$) bond is greater than energy released in the formation of nitrogen-oxygen bonds for two molecules of NO by an amount of 180.5 kJ. Hence formation of nitrogen oxide by the combination of nitrogen and oxygen is an endothermic reaction. In addition to these chemical

reactions, there are many physical processes which are exothermic and endothermic in nature.

When potassium nitrate is dissolved in water, cooling effect is felt. This is an endothermic process. When sodium hydroxide is dissolved in water, heating effect is felt. This is an exothermic process.



Evaporation or boiling of water, fusion or melting of ice are endothermic processes. During these processes, the absorbed heat energy is utilized in overcoming strong attractive forces (intermolecular forces) between water molecules. The reverse processes, crystallization and condensation are exothermic and release energy.

5-3 ELECTROLYSIS

Electricity involves flow of electrons through metals and movement of ions through solutions. Some substances dissolve in water and split into ions. These substances are called *electrolytes*. Ions are charged particles and possess certain electrical properties. The positively charged ions are known as *cations* and negatively charged ions are known as *anions*. We have already discussed in Unit 1 that when electricity is passed through water, oxygen is liberated at one electrode and hydrogen at the other. Similarly when electric current is passed through an acidified solution of copper (II) chloride, CuCl_2 , copper ions (Cu^{2+}) are attracted towards one electrode (cathode) and

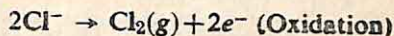
chloride ions (Cl^-) are attracted towards the other (anode). The process in which a chemical change is caused by passing an electric current through an electrolyte is known as *electrolysis*. The cell in which electrolysis is carried out is known as an *electrolytic cell*. The reactions that occur at the electrodes are oxidation-reduction reactions. In the electrolysis of $\text{CuCl}_2(aq)$ (Fig. 5-3), copper deposits at the cathode because the Cu^{2+} ions attract electrons and are reduced.

At the cathode :

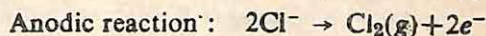
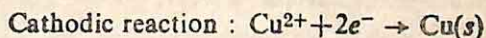


Simultaneously, the chloride ions move towards anode where two chloride ions lose two electrons and thereby are oxidized forming a molecule of $\text{Cl}_2(g)$.

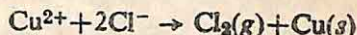
At the anode :



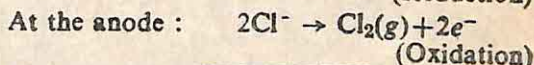
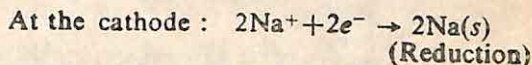
The net equation of an oxidation-reduction process occurring in an electrolytic cell is obtained by adding the reactions :



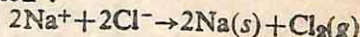
The net equation :



In the electrolysis of molten sodium chloride, sodium metal and chlorine gas are produced.



The net equation :



5-3-1 APPLICATIONS OF ELECTROLYSIS

Electrolysis is used in the production of certain metals and non-metals, purification of metals and in electroplating.

1. **Production of metals and non-metals :** Aluminium oxide from bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$) ore is dissolved in the molten mineral cryolite (Na_3AlF_6). The melt is subjected to electrolysis to form aluminium metal.

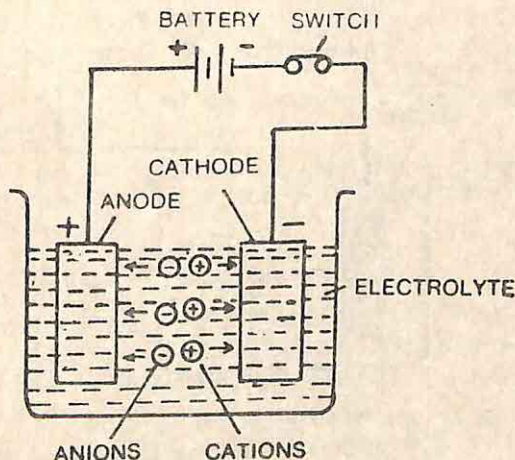


Fig. 5-3. An electrolytic cell. Electrolysis of cupric chloride solution

Electrolysis is carried out in an iron tank with a graphite lining which serves as the cathode. The anodes are carbon rods dipping in the fused electrolyte (Fig 5-4). During electrolysis the following reactions take place :

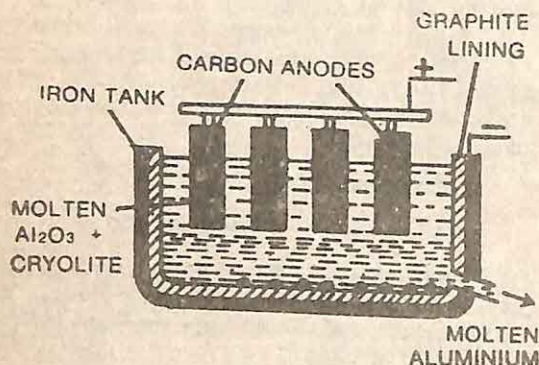
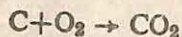


Fig. 5-4. Electrolytic preparation of aluminium.

At the cathode : $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}(s)$

At the anode : $2\text{O}^{2-} \rightarrow \text{O}_2 + 4e^-$

A part of oxygen escapes and rest of it oxidizes the carbon anodes, which are slowly eroded.



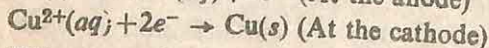
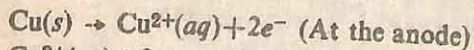
Magnesium chloride is melted and subjected to electrolysis to give magnesium metal.

At the cathode : $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}(s)$

At the anode : $2\text{Cl}^- \rightarrow \text{Cl}_2(g) + 2e^-$

The electrolysis of water gives hydrogen and oxygen gases.

2. Purification of metals : Electrolysis is used to purify metals. The process is known as *electrorefining*. Copper is electrorefined (Fig. 5-5) by making blister copper (impure copper) as anode and pure copper metal as cathode. Acidified copper sulphate is taken as electrolyte in the electrolytic cell. When electric current is passed, the Cu^{2+} ions from the solution move towards cathode and are deposited there. Cu from the anode goes into the solution producing Cu^{2+} ions.



This process is continued for several hours. During the process cathode increases in size and anode decreases in size. Very pure copper is produced at the cathode and sludge remains

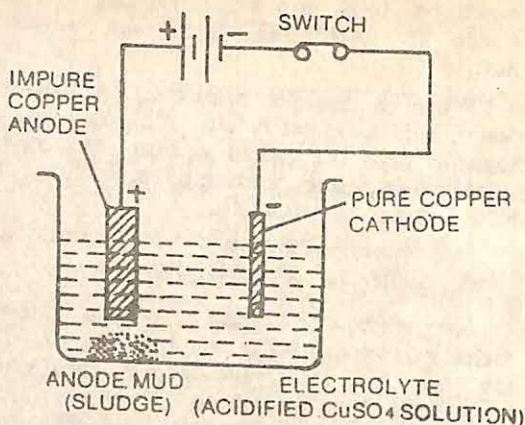
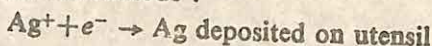


Fig. 5-5. Electrorefining of copper

at the anode. Metals like tin, aluminium, zinc, silver, etc. are refined electrolytically.

3. Electroplating. In electroplating a uniform layer of a metal is formed on the surface of an object. As shown in Fig. 5-6, the object to be electroplated is made cathode in the electrolytic cell and the plating metal is made anode. The electrolyte is a soluble plating metal salt. In the electroplating of silver on utensils, soluble silver salt is taken as the electrolyte. The electrode reactions are :

At the cathode :



At the anode :

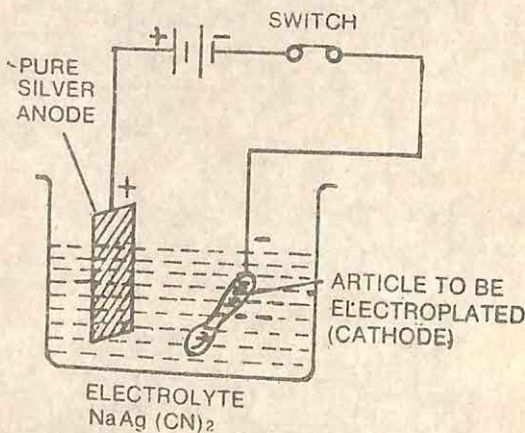
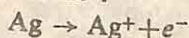


Fig. 5-6. Electroplating of silver

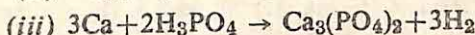
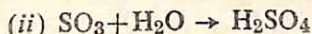
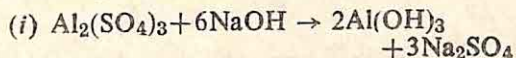
Metals like gold, chromium, nickel, platinum, etc. can be electroplated on the surfaces of iron

(steel) and copper. The electroplated objects resist corrosion. They can be used for decorative purposes.

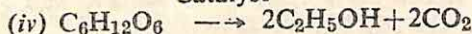
WORK EXERCISES

- What is a chemical reaction?
- (a) Name the various types of chemical reactions.

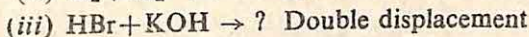
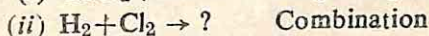
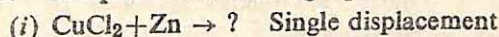
(b) Name the types of reactions with which the following equations are associated :



Catalyst

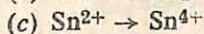
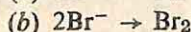
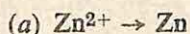


- Complete the following equations :



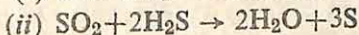
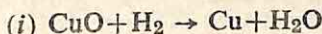
- (a) How does oxidation differ from reduction?

(b) Identify the following changes as oxidation or reduction :



- (a) What is a redox reaction?

(b) Identify the oxidizing and reducing agents in the following reactions :



- (a) Give an example of exothermic reaction.

(b) When ammonium chloride is dissolved in water cooling is produced. Name the type of the process.

- (a) What is electrolysis?

(b) Name three applications of electrolysis.

(c) Name one metal and one non-metal which are produced by electrolysis.

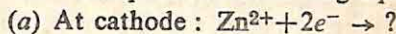
- (a) State the working of the object to be electroplated in the electrolytic cell.

(b) State the working of the object to be electrorefined in the electrolytic cell.

- (a) What is an electrolyte?

(b) What is an electrolytic cell?

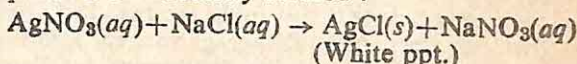
- Complete the following equations :



RATES OF CHEMICAL REACTION AND EQUILIBRIUM

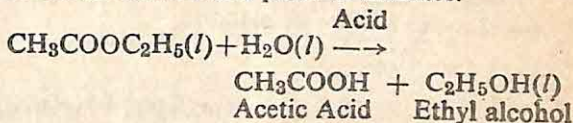
5-4. UNDERSTANDING OF RATE OF CHEMICAL REACTION

When a solution of silver nitrate is added to a sodium chloride solution, a white precipitate is immediately formed :

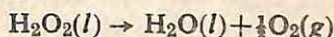


Thus, the reaction between silver nitrate (AgNO_3) and sodium chloride (NaCl) takes place very quickly or instantaneously.

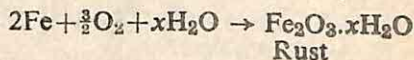
Hydrolysis of ethyl acetate in the presence of mineral acid takes place in minutes.



This is a slow reaction. Another example of such a reaction is the decomposition of hydrogen peroxide.



Iron nails when exposed to air and moisture get rusted. This process takes many days. In this process, a brown hydrated ferric oxide is formed on the surface of iron nails,



Another example of a very slow reaction is the formation of carbon dioxide when lumps of graphite are exposed to air,



This reaction takes many months/years.

We have seen that different reactions occur with different speeds. In every reaction, the concentration of reactants decreases and the concentration of products increases with time. The speed at which a reaction takes place can be expressed as the *rate of the reaction*. The rate of a chemical reaction is defined as the change in concentration of reactants or products per unit time.

$$\text{Rate of reaction} = \frac{\text{Change in concentration}}{\text{Time taken}}$$

For example, a reactant with concentration 4.0 moles/litre decomposes into products. After 10 minutes its concentration is measured to be 2.4 moles/litre. The rate of the decomposition reaction is given by

$$\begin{aligned}\text{Rate} &= \frac{(4.0 - 2.4) \text{ moles per litre}}{10 \text{ minutes}} \\ &= \frac{1.6}{10} \text{ mol litre}^{-1} \text{ min}^{-1} \\ &= 0.16 \text{ mol litre}^{-1} \text{ min}^{-1}\end{aligned}$$

The rate of a chemical reaction can be measured without disturbing the reaction itself. For example, the changing concentration of reactant or product with time may be determined by watching the changing colour intensity of the solution (if the products and reactants differ in colour) and by measuring the volume of the gas at different intervals of time (if a gas is liberated from solution). Thus we get the idea of rate of reaction.

In the reaction,



all the reactants and products are in the same phase. This is called a homogeneous reaction. In a heterogeneous reaction the reactants and products are in different phases. For example,



Here CaCO_3 and CaO are two solid phases and CO_2 is a gaseous phase.

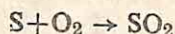
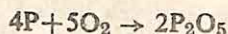
5-5. FACTORS AFFECTING THE RATE OF A REACTION

The rate of a reaction depends upon several factors. Since a reaction involves the breaking and forming of chemical bonds, the reacting particles must collide with each other, i.e., for a reaction to proceed, the atoms or molecules that compose the reactants, must collide with each other during their movement. Therefore, the rate of a reaction depends upon the number of collisions between the molecules of reactant. But mere collision of molecules is insufficient to cause a chemical reaction. Collisions between the slower particles are ineffective, i.e., they do not result in the breaking of old (reactant) bonds and the formation of new (product) bonds. Only the more energetic particles may undergo effective collisions, i.e., those that result in a chemical change. We shall now discuss some of the

factors which increase effective collisions among molecules of the reactants.

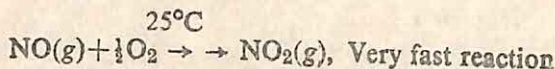
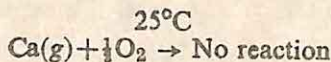
5-5-1. NATURE OF REACTANTS

A match stick burns instantaneously whereas a piece of charcoal takes time to burn. Phosphorus and sulphur combine with oxygen in the air to form oxides.



Phosphorus burns vigorously in air. Sulphur is first ignited then only burns in air. The difference in the readiness of their reactions must be due to difference in the arrangements of the atoms of the two elements (P and S) and the nature of bonds between them.

Nature of chemical bonds between the constituent elements of reactants also decide the rate of a reaction.



Sodium metal if placed in moist air, will burn immediately. Iron will rust slowly in moist air.

5-5-2. CONCENTRATION OF REACTANTS

Substances burn much more rapidly in pure oxygen than in air. Zinc reacts with hydrochloric acid with the evolution of hydrogen gas. The reaction becomes faster in increasing the concentration of hydrochloric acid. Increasing the concentration of any one or all of the reactants increases the number of molecular collisions. In other words the probability of a reaction increases as the number of reacting particles per unit volume increases. Increased reactant concentration results in increased reaction rate.

Experiment 5-1. Take one gram marble chips in one test tube and two gram marble chips in the second test tube. Add dilute hydrochloric acid in the first test tube and concentrated hydrochloric acid in the second test tube (Fig. 5.7). Reaction starts with the evolution of carbon dioxide gas. We shall observe that carbon dioxide gas will be evolved more rapidly from the second test tube which contains higher concentration of reactants.

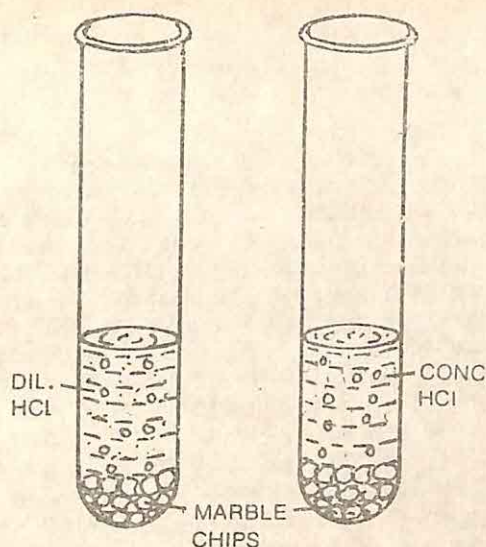
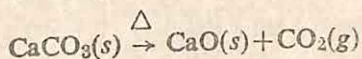


Fig. 5.7. Effect of concentration of reactants on rate of reaction

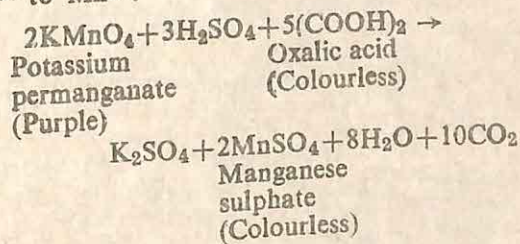
5-5-3. EFFECT OF TEMPERATURE

An increase in temperature results in an increase in reaction rate. The rate of a reaction is approximately doubled for each 10°C increase in temperature. Calcium carbonate on heating decomposes into calcium oxide and carbon dioxide gas.



Carbon dioxide is evolved more rapidly if CaCO_3 is heated at a higher temperature.

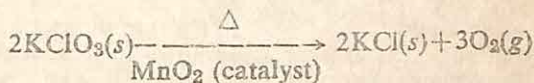
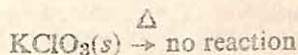
When acidified solution of potassium permanganate is added to cold oxalic acid solution no appreciable reaction is observed, KMnO_4 imparts its own colour to the solution. But if this solution is heated, the purple colour disappears quickly. In this reaction, KMnO_4 oxidizes oxalic acid and itself reduced from Mn^{7+} to Mn^{2+} .



5-5-4. EFFECT OF CATALYST

A catalyst is a substance that changes the rate of a reaction without itself undergoing any

permanent change in the process. Potassium chlorate (KClO_3) on heating does not produce oxygen. But a mixture of manganese dioxide and potassium chlorate on heating produces oxygen.

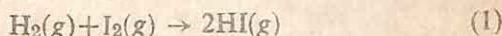


Here MnO_2 acts as a catalyst and increases the rate of reaction. The quantity of manganese dioxide was found unchanged after the process.

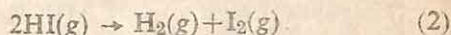
Vanadium pentoxide (V_2O_5) is used as a catalyst in the manufacture of sulphuric acid. Iron is used as a catalyst in the manufacture of ammonia by Haber's process. Nickel is used in the manufacture of vanaspathi ghee. Catalysts which act in human body are called 'enzymes'.

5-6. CHEMICAL EQUILIBRIUM

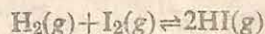
A gaseous mixture of hydrogen and iodine, in a closed vessel, will react to form hydrogen iodide at 713K :



Pure hydrogen iodide at the same temperature would have decomposed to give hydrogen and iodine:



Now, the HI is formed in reaction (1) by the combination of H_2 and I_2 . The HI is decomposed in reaction (2) into H_2 and I_2 at the same temperature. Thus, in a mixture of the three gases H_2 , I_2 and HI , both reaction (1) and (2) will take place. This fact is expressed by saying that reaction (1) or (2) is *reversible*. Reaction (1) and (2) can be written in a combined form by introducing a sign of double arrow ($\rightleftharpoons$)



or



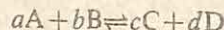
Whatever appears on the left hand side of the equation is called a 'reactant' and whatever appears on the right hand side of the equation is called a 'product'. A reaction is said to go forward when it goes from left to right. Sign ($\rightarrow$) indicates forward direction. A reaction is said to go in 'backward' or in 'reverse' direction when it goes from right to left. Sign ($\leftarrow$) indicates backward or reverse reaction.

The rate of a reaction increases as the concentration of the reactants increases and it decreases as the concentration of reactants decreases. If reaction (1) is occurring the concentration of each H_2 and I_2 will decrease and that of HI increases. After some time the hydrogen iodide also start decomposing to give back hydrogen and iodine i.e., reaction (2). The rate of reaction (1) slows down, while rising concentration of HI speeds up the rate of backward reaction. Conversely if reaction (2) is occurring decrease in concentration of HI will slow down the rate of reaction (2), and increase in concentration of each H_2 and I_2 will speed up the backward reaction. A state of *equilibrium* will eventually be reached when the forward and the reverse reactions are occurring at the same rate. This type of equilibrium that exists between opposing chemical reactions is called *chemical equilibrium*. Since the conversion of reactants into products and of products into reactants continues even after equilibrium is attained the equilibrium is also called *dynamic equilibrium*. There will be no further net change in the composition of the reaction mixture unless some external disturbance is imposed. When

a reaction reaches equilibrium, the final amounts of reactants and products need not be equal. Thus, equilibrium means that only the rates of reactant formation and product formation are the same.

Figure 5.8 shows how the reaction $H_2 + I_2 \rightleftharpoons 2HI$ approaches equilibrium. The horizontal axis represents the time in minutes. The vertical axis represents composition of the reaction mixture. If we start at the bottom with $H_2 + I_2$, the amount of HI formed increases rapidly in the first instance and then decreases slowly approaching a value around 78%. If we start at the top with pure HI , the same equilibrium state is reached. Now, the rate of forward reaction is equal to the rate of backward reaction.

An *equilibrium constant*, K , is associated with every reversible reaction that reads equilibrium. The equilibrium constant is equal to the ratio of the equilibrium concentrations of the products over the equilibrium concentrations of the reactants. This ratio is always the same for a particular reaction at a given temperature. For the general reaction,



where A and B are reactants, C and D are products, and a, b, c and d are coefficients in the balanced equation. The equilibrium constant is given by the following expression :

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Square brackets indicate concentrations of reactants and the products in moles/litre. Thus, for the synthesis of ammonia, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the equilibrium constant expression is :

$$K = \frac{[NH_3]^2}{[N_2] [H_2]^3}$$

5-6 LE-CHATELIER'S PRINCIPLE

There are three main factors which change the state of equilibrium. These are concentration, temperature and pressure. Catalysts do not affect the composition of equilibrium mixture. A catalyst only changes the rate of a reaction. Equilibrium is attained quickly in the presence of a catalyst.

The French chemist, Henry Louis Le Chatelier (1850-1926) formulated a principle governing equilibrium. *Le-Chatelier's principle* states that when a change is made in the concentration, temperature or pressure of an equilibrium mixture, the equilibrium shifts in direction that tends to oppose the change.

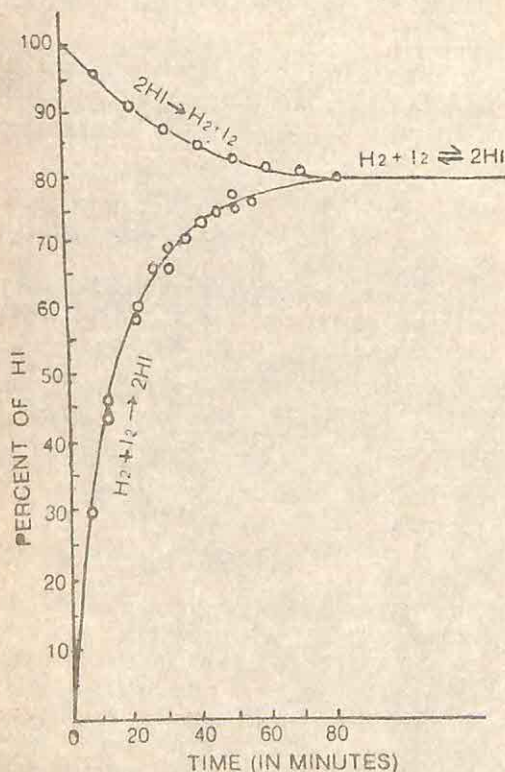
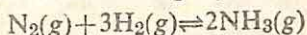


Fig. 5-8 Experimental data on the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI$ at 713 K.

Now we shall discuss the effect of these factors on equilibrium state of a reaction.

5-6-1 EFFECT OF CHANGE OF CONCENTRATION

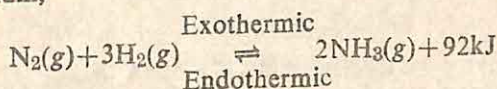
Consider the following equilibrium



Suppose some H_2 is added to the equilibrium, the equilibrium will shift towards right. Similarly, addition of N_2 causes a shift to the right, and addition of NH_3 causes a shift to the left. The general rule is that increase in the concentration of one substance in an equilibrium mixture displaces the equilibrium in that direction which consumes some of the added material. Decrease in the concentration of a substance causes the production of more and more of that substance. This property is utilized in chemical industries to get better yield.

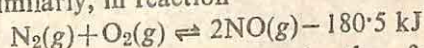
5-6-2 EFFECT OF CHANGE IN TEMPERATURE

Consider the following reaction at equilibrium,



The forward reaction is exothermic and the backward reaction is endothermic. In applying Le-Chatelier's principle to predict the effect of change in temperature on the equilibrium, the general rule is, increase in the temperature causes reaction to occur in that direction which results in absorption of heat, and decrease in the temperature causes reaction to occur in the direction which results in the evolution of heat. Therefore, decrease of temperature in the above reaction shifts equilibrium towards right, i.e., favours formation of ammonia.

Similarly, in reaction

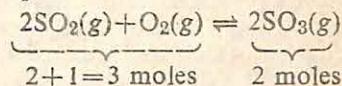


if temperature is increased the forward reaction is favoured. Now we conclude that formation of ammonia is favoured at low temperature and formation of nitric oxide is favoured at high temperature.

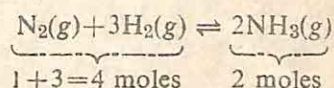
Forward reaction	Reverse reaction	Favoured by increased temperature	Favoured by decreased temperature
1. exothermic	endothermic	reverse	forward
2. endothermic	exothermic	forward	reverse

5-6-3 EFFECT OF CHANGE IN PRESSURE

The rule is that increase in the pressure on the reaction in equilibrium favours that reaction which produces less moles of gas. For example, the combination of sulphur dioxide and oxygen to give sulphur trioxide

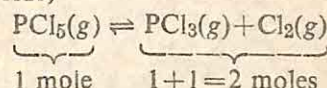


is accompanied by a decrease in number of moles. According to Le-Chatelier's principle, therefore, a high pressure would give a better yield of sulphur trioxide. Similarly, the formation of ammonia



is accompanied by a decrease in the number of moles. If the pressure is increased volume will decrease. Thus, increase in production of ammonia is observed at higher pressure.

Consider the dissociation of phosphorus pentachloride,



The forward reaction is accompanied by the increase in number of moles. According to Le-Chatelier's principle the dissociation of phosphorus pentachloride is suppressed with increase of pressure.

Other reactions that illustrate the effect of change in pressure are the following :

Reaction	Direction favoured by increased pressure
$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$	reverse (←)
$2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$	forward (→)
$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$	neither

The following table summarizes the effects on the synthesis of ammonia discussed in this section :

Change	Reaction favoured
add N_2 or H_2	forward (→)
add NH_3	reverse (←)
remove N_2 or H_2	reverse (←)
remove NH_3	forward (→)
increase pressure	forward (→)
decrease pressure	reverse (←)
increase temperature	reverse (←)
decrease temperature	forward (→)

Le-Chatelier's Principle and Physical Equilibrium. Consider a sample of liquid in a closed container as shown in Fig. 5-9. The liquid will change into vapours by the absorption of heat. Conversion of vapours into liquid is accompanied by evolution heat. The evaporation process and the condensation process begin to act in opposition to one another. A situation in which two processes are acting in equal and opposite manners is called a state of dynamic equilibrium

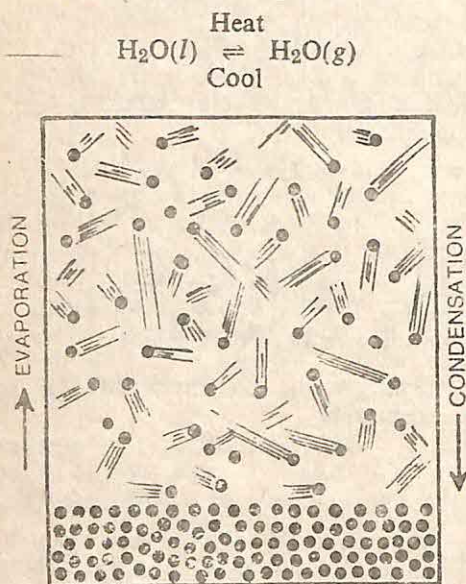


Fig. 5-9 Evaporation of liquid molecules and condensation of vapour molecules occur continuously. When the rates of evaporation and condensation are equal, it is in a state of dynamic equilibrium.

According to Le-Chatelier's principle, addition of heat to such a system will shift the equilibrium towards right. Increase of temperature, increases vapour pressure on the system. Thus, the vapour pressure of a liquid increases with rise in temperature.

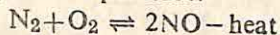
WORK EXERCISES

- (a) Define rate of a reaction.
(b) What are the various factors which influence the rate of reactions?
- (a) What will happen to the rate of reaction with increase in temperature?
(b) Give one example of a reaction in which catalyst increases the rate of reaction.
(c) How does the rate of a reaction change with increase in concentration of reactants?

3. Dilute sulphuric acid reacts with a metal 'M' to produce hydrogen. Suggest a way to increase the rate of formation of hydrogen by this method.

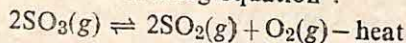
- What is a reversible reaction?
- What do you mean by forward and backward reaction?
- What is chemical equilibrium?
- What is the relation between forward and backward rates of reaction at equilibrium?
- State Le Chatelier's principle in your own words.

9. (a) For the following reaction, state in which direction the equilibrium will shift on increasing the temperature.

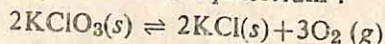


(b) List the factors which influence the state of chemical equilibrium.

10. (a) Predict the influence of increase in pressure on the following equation :



(b) What is the effect of removing O_2 in the following reaction at equilibrium?



IONIC EQUILIBRIUM AND THE pH SYSTEM

5-7 ELECTROLYTES AND NON-ELECTROLYTES

Substances which furnish ions in solution and conduct electricity are called *electrolytes*. For example, NaCl , CuSO_4 , NaNO_3 , HCl , KOH , etc., are electrolytes. The substances which do not furnish ions in solution, and hence, do not conduct electricity are called *non-*

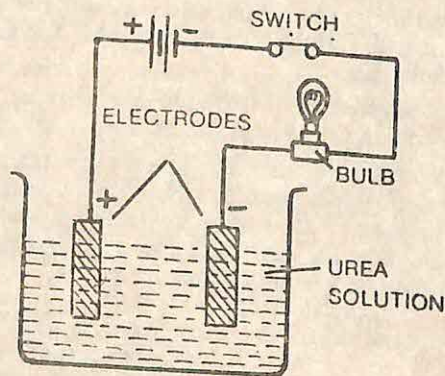


Fig. 5-10 (a) Urea solution in water is a non-conductor of electricity

electrolytes. For example, sugar, CCl_4 , CH_3OH , urea, etc., are non-electrolytes. An electrolyte is distinguished from a non-electrolyte by performing the experiment as shown in Fig 5-10. The solution of the compound to be tested is taken in a beaker. If the compound is non-electrolyte, the bulb does not glow (Fig 5-10 a). In case the bulb glows, it means that solution conducts electricity (Fig. 5-10 b) and the compound is an electrolyte.

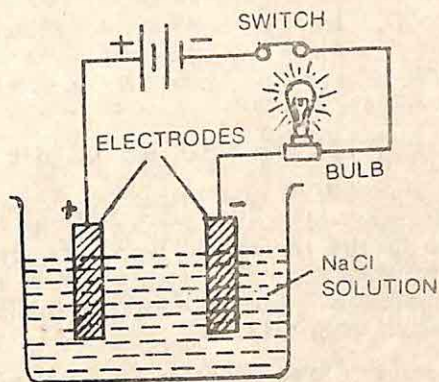


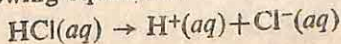
Fig. 5-10 (b) Sodium chloride solution is a conductor of electricity

5-8 STRONG AND WEAK ELECTROLYTES

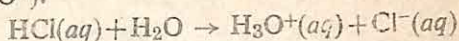
Substances, like sodium chloride that separate completely into ions, conduct electricity well and are said to be *strong electrolytes*. Other examples of strong electrolytes are, KCl , NaOH , HNO_3 , CuSO_4 , etc. Substances, that do not dissociate completely in solution, conduct electricity poorly and are called *weak electrolytes*, e.g., NH_4OH , CH_3COOH , H_2S , etc. The apparatus shown in Fig. 5-10 can also be used to distinguish between strong and weak electrolytes. If the experiment is performed with various electrolytes it will be seen that the bulb glows very brightly with strong electrolytes and less brightly with weak electrolytes.

5-9 ACIDS AND BASES

The Swedish chemist Swante Arrhenius studied the dissociation of electrolytes. In 1884, he defined an acid as an electrolyte that furnishes H^+ ions. If dissociation is complete, it is a strong acid. For example, HCl , HNO_3 , H_2SO_4 , and HBr are strong acids. Hydrochloric acid ionizes in water according to the following equation:

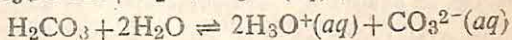
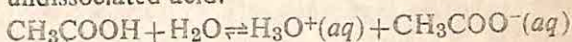


The hydrogen ion, H^+ (a proton) interact with water molecules to give hydronium ions (H_3O^+).

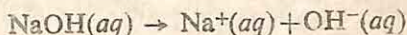


An acid has sour taste, dissolves certain metals and turns blue litmus red.

Many acids dissociate partially in water solution. These are called weak acids, e.g., CH_3COOH , H_2CO_3 , HNO_2 , H_2SO_3 , etc. An equilibrium exists between dissociated and undissociated acid.



Arrhenius defined a base as an electrolyte that furnishes OH^- ions in water solution. For example, sodium hydroxide and potassium hydroxide are bases.



Their dissociation is large enough in water solution. Thus they are also called strong bases. Bases have bitter taste, feel slippery to the touch and change red litmus to blue. Ammonium hydroxide dissociates to a small extent in water. So, it is an example of a weak base.



Water soluble bases are called alkalis e.g., NaOH , KOH , $\text{Ba}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc.

5-10 IONIZATION OF WATER

Water ionizes to an extremely small extent. The equation for its ionization may be written



Since it is an ionic equilibrium, we can write the ionization constant expression,

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

From the equation for the ionization of water, one can see that each H_2O molecule gives one H^+ ion and one OH^- ion. $[\text{H}^+]$ and $[\text{OH}^-]$ in pure water at 25°C have been determined experimentally to be 1×10^{-7} M each. So we can conclude that $[\text{H}_2\text{O}]$ is a constant. Therefore,

$$K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{[\text{H}^+][\text{OH}^-]}{\text{Constant}}$$

$$\text{or } K \times \text{Constant} = K_w = [\text{H}^+][\text{OH}^-]$$

This constant, K_w is called the *ionic product of water*. At 298 K, the value of K_w is

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-7} \times 10^{-7} = 10^{-14}$$

In water and in all aqueous solutions, this equilibrium, $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ exists.

Therefore, $1 \times 10^{-14} = [\text{H}^+] \times [\text{OH}^-]$

and $[\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}^-]}$ or $[\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}^+]}$

5-11 THE pH SYSTEM

An acidic solution is one in which the concentration of H^+ ions exceeds that of OH^- ions, i.e.,

$[\text{H}^+] > [\text{OH}^-]$; $[\text{H}^+] > 10^{-7}\text{M}$; $[\text{OH}^-] < 10^{-7}\text{M}$

In basic solution, there are more OH^- ions than H^+ ions, i.e.,

$[\text{OH}^-] > [\text{H}^+]$; $[\text{OH}^-] > 10^{-7}\text{M}$; $[\text{H}^+] < 10^{-7}\text{M}$

We have seen that it is possible to describe acidity or basicity of a solution by specifying the concentration of H^+ ions. A Danish biochemist, Peter Sorensen, in 1909, proposed a new system, known as pH scale. He defined pH as follows:

$$\text{pH} = -\log[\text{H}^+] = \log \frac{1}{[\text{H}^+]}$$

The small p in pH is derived from the German word 'potenz' meaning power. Thus pH means power of hydrogen ion.

In the same way, one can define the pOH as follows:

$$\text{pOH} = -\log[\text{OH}^-]$$

The pH and pOH of any solution are related to one another as follows:

$$\text{pH} + \text{pOH} = 14$$

So, if either the pH or pOH of a solution is known, the other can be found by subtracting from 14.

To differentiate between neutral, acidic and basic solutions, one can make this distinction in terms of pH,

Neutral solution: $[\text{H}^+] = 10^{-7}\text{M}$ pH = 7.0
Acidic solution: $[\text{H}^+] > 10^{-7}\text{M}$ pH < 7.0
Basic solution: $[\text{H}^+] < 10^{-7}\text{M}$ pH > 7.0

Acidity and basicity on the pH scale are as given in Fig. 5.11.

A solution becomes more and more acidic if its pH decreases below 7. It becomes more and more basic if its pH increases above 7. Table 5-2 lists the pH of some common solutions.

Table 5-2 The pH values of some common solutions

Solution	pH	Solution	pH
Gastric juices	1.0–3.0	Milk	6.3–6.6
Lemon juices	2.2–2.4	Saliva	6.5–7.5
Vinegar	2.4–3.4	Blood	7.3–7.5
Wine	2.8–3.8	Sea-water	8.4
Black coffee	4.8–5.2	Soap solution	8.5–10.0

5-11-1 IMPORTANCE OF pH VALUE

pH value finds its vital role in agriculture. The pH value of a soil decides the manure required for that soil and the crop to be sown. Plants do not grow well in soil which is too acidic or alkaline. Choice of artificial fertilizer also depends upon pH of soil.

pH value is also an important factor in biological processes. Most of the bacteria grow best in neutral or slightly alkaline solution. By determining the pH value, we can adjust the medium of many biological processes like fermentation, enzyme hydrolysis, sterilization, etc. Fluids of the body like blood, urine and lymph undergo very little change in pH. A very small variation in the pH of blood gives a lot of body ache. Too much spicy food sometimes causes unpleasant feeling. This is due to excess stomach acidity; one way to relieve the situation is to take an antacid tablet or antacid solution.

Water, containing pollutant chemicals, if used for irrigation purposes destroys crops, causes death to animals in lakes and rivers, corrodes metals if immersed in it. This is because pollutant chemicals change acidity or alkalinity of water.

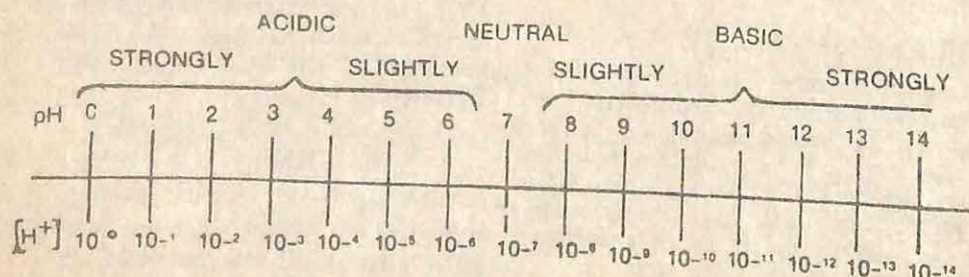


Fig. 5-11. The pH scale between 0 and 14.

pH value is of great importance in analytical chemistry. Cations of group IInd are precipitated as sulphides in acidic medium while cations of group IVth are precipitated as sulphides in alkaline medium.

Solved Numericals

5-1. Calculate (a) the pH of a solution of $[H^+] = 0.001 \text{ M}$.

(b) the pH of a solution of $[OH^-] = 10^{-9} \text{ M}$.

Solution :

$$(a) [H^+] = 0.001 \text{ M} = \frac{1}{1000} \text{ M} \\ = 10^{-3} \text{ M}$$

$$\text{Therefore, } pH = -\log 10^{-3} = 3$$

$$(b) [OH^-] = 10^{-9} \text{ M}$$

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

$$\text{or } [H^+] = \frac{1 \times 10^{-14}}{[OH^-]} = \frac{1 \times 10^{-14}}{10^{-9}} \\ = 10^{-14+9} = 10^{-5} \text{ M}$$

$$pH = -\log [H^+] = -\log 10^{-5} = 5.$$

5-2. Calculate (a) $[H^+]$, and (b) $[OH^-]$ of a solution of $pH = 4$.

Solution

$$pH = -\log [H^+] = \log \frac{1}{[H^+]}$$

$$4 = -\log [H^+] = \log \frac{1}{[H^+]}$$

$$\text{or } \log \frac{1}{[H^+]} = 4 = \log 10^4$$

taking antilog on both sides,

$$\frac{1}{[H^+]} = 10^4$$

$$\text{or } [H^+] = \frac{1}{10^4} = 10^{-4} \text{ M}$$

and

$$[OH^-] = \frac{1 \times 10^{-14}}{10^{-4}} = 10^{-10} \text{ M}$$

WORK EXERCISES

1. What is the difference between an electrolyte and a non-electrolyte? Give examples.

2. How will you distinguish between weak and strong electrolytes?

3. Classify the following electrolytes into weak and strong electrolytes :

NaCl , KNO_3 , CH_3COOH , NH_4OH , $\text{Ca}(\text{OH})_2$, H_2SO_4 , HCl , H_2CO_3 , H_2S and AgNO_3 .

4. Define an acid and a base.

5. What is pH scale?

6. What is hydronium ion?

7. The pH of water is 7. What is the H^+ ion concentration of water?

8. Which will have higher pH value, a strong acid or a strong base?

9. What will be the concentration of hydronium ion in the following solutions?

(a) 10^{-4} M HCl (b) 10^{-2} M HNO_3

(c) $10^{-3} \text{ M H}_2\text{SO}_4$

[Ans. (a) 10^{-4} M , (b) 10^{-2} M ,
(c) $2 \times 10^{-3} \text{ M}$]

10. Calculate the $[OH^-]$ of the following solutions :

(a) $pH = 2$ (b) $pH = 6$

(c) $pH = 9$ (d) $pH = 12$

[Ans. (a) 10^{-12} M , (b) 10^{-8} M ,
(c) 10^{-5} M , (d) 10^{-2} M]

KEY TERMS

5-1 **Chemical reaction.** Substance or a group of substances is changed into one or more different substances.

5-2 **Combination reaction.** Chemical reaction in which two or more substances unite to form a single product, $A + B \rightarrow AB$.

5-3 **Decomposition reaction.** Reaction in which a single reactant is decomposed or broken down into two or more products, $AB \rightarrow A + B$.

5-4 **Oxidation.** Loss of one or more electrons by an atom, a group of atoms or ion.

- 5-5 **Reduction.** Gain of one or more electrons by an atom, a group of atoms or ion.
- 5-6 **Oxidizing agent.** A substance which can oxidize other substances by accepting electrons.
- 5-7 **Reducing agent.** A substance which can reduce other substances by supplying electrons.
- 5-8 **Redox reaction.** A reaction in which both reduction and oxidation take place simultaneously.
- 5-9 **Exothermic reaction.** A reaction which takes place with the evolution of heat.
- 5-10 **Endothermic reaction.** A reaction which takes place with the absorption of heat.
- 5-11 **Electrolysis.** Decomposition of a substance by passage of an electric current through an electrolytic cell.
- 5-12 **Electrolyte.** Substance, such as sodium chloride, which conducts electricity when dissolved in water.
- 5-13 **Ion.** An atom or a group of atoms of molecule that has gained or lost one or more electrons.
- 5-14 **Ionization.** The process of decomposition of an ionic compound in solution into its ions.
- 5-15 **Strong electrolytes.** Electrolytes capable of complete or almost complete ionization in solution.
- 5-16 **Weak electrolytes.** Electrolytes that are only partially ionized in solution.
- 5-17 **Anode.** Electrode at which oxidation occurs in an electrolytic cell.
- 5-18 **Cathode.** Electrode at which reduction occurs in an electrolytic cell.
- 5-19 **Cations.** Positive ions that go to the cathode during electrolysis.
- 5-20 **Anions.** Negative ions that go to the anode during electrolysis.
- 5-21 **Electrorefining.** Refining of metals such as copper, tin, silver, etc., with the help of an electric current.
- 5-22 **Electroplating.** Deposition of one metal over another with the help of an electric current.
- 5-23 **Rate of reaction.** Change of concentration (number of moles per unit volume) per unit time of one of the reactants or products in the reaction.
- 5-24 **Reversible reaction.** A reaction which can proceed in both the directions.
- 5-25 **Irreversible reaction.** A reaction in which reactant or reactants cannot be obtained from the products under any conditions.
- 5-26 **Chemical equilibrium.** A state when the rates of the forward and the backward reactions are the same.
- 5-27 **Catalyst.** A substance which alters the speed of a chemical reaction without itself undergoing any chemical change.
- 5-28 **Le-Chatelier's principle.** If a system in chemical equilibrium is altered in any way, the system will respond in such a way as to minimise the effect of that change.
- 5-29 **Ionic product of water.** Product of the concentrations of H^+ and OH^- ions in water ($K_w = [H^+][OH^-]$).
- 5-30 **pH.** A measure of acidity or alkalinity of a solution. pH is the negative logarithm to base 10 of the H^+ ion concentration in moles per litre ($pH = -\log[H^+]$).

UNIT THROUGH EXERCISES

5-1 Given the following equations, label each as a combination, decomposition or single displacement reaction :

- (a) $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$
 (b) $\text{F}_2 + 2\text{NaI} \rightarrow 2\text{NaF} + \text{I}_2$
 (c) $4\text{Fe} + 3\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$
 (d) $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
 (e) $\text{Na} + \text{AgNO}_3 \rightarrow \text{Ag} + \text{NaNO}_3$
 (f) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 (g) $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$
 (h) $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$

[Ans. (a), (b), (d), (e) are single displacement reactions

(c), (g) are combination reactions

(f), (h) are decomposition reactions]

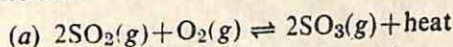
5-2. Which of the following reactions are redox reactions? Identify the oxidizing agent and the reducing agent in the redox reaction.

- (a) $\text{I}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow 2\text{HI}(\text{g}) + \text{S}(\text{s})$
 (b) $\text{Pb}^{2+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \rightarrow \text{PbI}_2(\text{s})$
 (c) $\text{SO}_2(\text{aq}) + \text{NO}_2(\text{aq}) \rightarrow \text{SO}_3(\text{aq}) + \text{NO}(\text{aq})$
 (d) $\text{NH}_3(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq})$
 (e) $2\text{Cl}_2(\text{g}) + \text{CH}_4(\text{g}) \rightarrow 4\text{HCl}(\text{g}) + \text{C}(\text{s})$

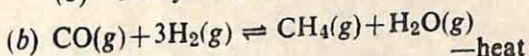
[Ans. Oxidizing agent Reducing agent

- (a) I_2 H_2S
 (c) NO_2 SO_2
 (e) Cl_2 CH_4

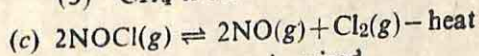
5-3. Indicate an equilibrium shift, right (forward) or left (backward), in the following reactions :



- (1) temperature is increased
 (2) pressure is reduced
 (3) catalyst is added



- (1) temperature is lowered
 (2) pressure is increased
 (3) CH_4 is removed from the system



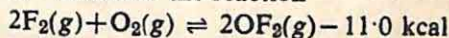
- (1) temperature is raised
 (2) pressure is increased
 (3) extra chlorine gas is added

[Ans. (a) (1) backward (2) backward
 (3) no effect

(b) (1) backward (2) forward
 (3) forward

(c) (1) forward (2) backward
 (3) backward]

5 4. Consider the reaction



What effect does,

(a) Increasing the temperature have on $[\text{OF}_2]$?

(b) Increasing the pressure have on $[\text{F}_2]$?

(c) Adding a catalyst have on $[\text{OF}_2]$?

(d) Adding a catalyst have on the value of K_{eq} ?

(e) Decreasing the temperature have on $[\text{OF}_2]$?

(f) Decreasing the $[\text{F}_2]$ have on the point of equilibrium?

[Ans. (a) $[\text{OF}_2]$ increases (b) $[\text{F}_2]$ decreases

(c) no effect (d) no effect

(e) $[\text{OF}_2]$ decreases (f) shifts left

5-5. Identify each of the following solutions as acidic, basic or neutral

(a) $\text{pH}=2$ (b) $\text{pOH}=6$

(c) $\text{pH}=9$ (d) $\text{pOH}=14$

(e) $[\text{H}^+]=10^{-7}\text{M}$ (f) $\text{pOH}=9$

(g) $\text{pH}=0$ (h) $\text{pH}=3.5$

(i) $[\text{H}^+]>10^{-7}\text{M}$ (j) $[\text{OH}^-]=10^{-7}\text{M}$

(k) $\text{pH}=11.3$ (l) $[\text{OH}^-]<10^{-7}\text{M}$

(m) $\text{pOH}=2.7$ (n) $\text{pOH}=13$

(o) $[\text{OH}^-]>10^{-7}\text{M}$ (p) $[\text{H}^+]<10^{-7}\text{M}$

(q) $\text{pH}=7$ (r) $\text{pOH}=7$

[Ans. Acidic : a, d, f, g, h, i, l, n

Basic : b, c, k, m, o, p

Neutral : e, j, q, r].

5-6. Choose the true statements in the following :

- In the reaction, $\text{Fe} + \text{S} \rightarrow \text{FeS}$, S is the oxidizing agent and Fe is reduced.
- Positive ions migrate to the cathode in electrolytic cells and are called cations.
- The positive electrode in an electrolytic cell is called cathode.

- In oxidation-reduction reactions, the number of electrons lost or gained must be equal.
- Acids taste sour and bases taste bitter.
- A solution whose $\text{pH}=2$ is less acidic than a solution whose $\text{pH}=5$.
- If the $[\text{H}^+]=1 \times 10^{-6}\text{M}$, its $\text{pOH}=1 \times 10^{-1}$.
- If the pOH of a solution is 11, its pH is 3.
- An increase in temperature always results in an increase in reaction rate.
- One of the most important factors in determining the rate of reaction is the nature of reactants.

[Ans. 2, 4, 5, 8, 9, 10 are true].

Multiple Choice Questions

5-7. Put a (✓) mark against the most appropriate choice :

- Which of the following expressions will give the pH of an aqueous solution in terms of the hydrogen ion concentration ?

(a) $\log [\text{H}^+]$ (b) $\frac{K_w}{[\text{OH}]}$
 (c) $-\log [\text{H}^+]$ (d) $-\log \frac{1}{[\text{H}^+]}$

- Which of the following gives the pH of an aqueous solution of 0.001 M HCl ?

(a) -3 (b) 11
 (c) 3.5 (d) 3

- Which of the following gives the pH of an aqueous solution of 0.001 M NaOH

(a) -11 (b) -3
 (c) 3 (d) 11.

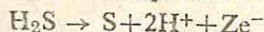
- The chemical reaction which takes place at the anode (positive electrode) in electrolysis is :

(a) Oxidation (b) Reduction
 (c) Hydrolysis (d) Dissociation

- Which of the following is an oxidation process ?

(a) The increase in positive charge of an ion.
 (b) The removal of hydrogen from a compound.
 (c) The addition of chlorine to a compound.
 (d) The loss of hydrogen ions by an acid.

- To balance the equation



the value of Z is given by

(a) 1 (b) 2 (c) 3 (d) 4

- The reaction $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{NaNO}_3 + \text{AgCl}$ is known as :

(a) Redox reaction
 (b) Double decomposition reaction
 (c) Combination reaction
 (d) Reversible reaction

- At the equilibrium state :

(a) Rate of forward direction is greater than rate of backward direction.
 (b) Rate of backward direction is greater than rate of forward direction.
 (c) Rate of forward direction is equal to rate of backward direction.
 (d) None of the above

- A catalyst is a substance that

(a) increases the yield.
 (b) alters the rate of reaction.
 (c) takes part in a chemical reaction.
 (d) all of the above.

- In reductions process the electron are :

(a) gained (b) lost (c) exchanged
 (d) neither gained nor lost

[Ans. 1. (c), 2. (d), 3. (d), 4. (a), 5. (a), 6. (b), 7. (b), 8. (c), 9. (b), 10. (a)]

5-8. Fill in the blanks

- A reaction that evolves heat is called an..... reaction.
- A reaction that absorbs heat is called an..... reaction.
- A..... is a substance that alters the rate of a reaction without being used up in the reaction.
- Equilibrium occurs when two opposing reactions are occurring..... and at the same.....
- A strong acid is one that is..... ionized.
- An acid turns..... litmus....., whereas a base turns..... litmus.....
- An acid is a proton..... and a base is a proton.....
- $\text{pH} = \dots\dots\dots [\text{H}^+]$.
- The process whereby electrical energy is used to bring about a chemical reaction is called.....

10. electrolytes are completely dissociated in aqueous solution.
11. The pH value of an alkaline solution is.....7.
12. A positively charged ion is called.....
13. An article to be electroplated is made in the electrolytic cell.

14. During electrolysis, oxidation takes place at whereas reduction takes place at.....

[Ans. 1. exothermic, 2. endothermic, 3. catalyst, 4. simultaneously, rate, 5. completely, 6. blue, red, red, blue, 7. donor, acceptor, 8. -log, 9. electrolysis, 10. strong, 11. greater than, 12. cation, 13. cathode, 14. anode, cathode].

5-9. Match the terms in column A with the descriptions in column B.

Column A

1. Chemical reaction
2. Chemical equation
3. Reactant
4. Product
5. Catalyst
6. Reaction rate
7. Reversible reaction
8. Chemical equilibrium
9. Reducing agent
10. Oxidising agent
11. Anode
12. Cathode

Column B

- (a) change in concentration with time.
- (b) reduction occurs here.
- (c) process of chemical change.
- (d) goes in both directions.
- (e) oxidation occurs here.
- (f) short hand representation of reaction.
- (g) speeds up reaction.
- (h) accepts electrons.
- (i) starting substance.
- (j) forward and backward reaction rates are equal.
- (k) substance produced
- (l) donates electrons.

REVIEW QUESTIONS

5-1 Define : Equation, reactant and product.

5-2 Explain the meaning and use of each of the following symbols :

- (a) $\rightarrow$, (b) $\rightleftharpoons$, (c) $\uparrow$,
 (d) $\downarrow$, (e) (g), (f) Δ ,
 (h) (s).

5-3 Complete and balance the following equations :

A. Combination

1. Zinc + sulphur $\xrightarrow{\quad}$
2. Iron + sulphur $\xrightarrow{\quad}$
3. Aluminium + oxygen gas $\xrightarrow{\quad}$
4. Sodium + chlorine gas $\xrightarrow{\quad}$

B. Decomposition

1. Mercury (II) oxide $\xrightarrow{\Delta}$
2. Copper (II) carbonate $\xrightarrow{\Delta}$

3. Potassium chlorate $\xrightarrow{\Delta}$

4. Calcium carbonate $\xrightarrow{\Delta}$

C. Single displacement

1. Zinc + sulphuric acid $\longrightarrow$
2. Aluminium + hydrochloric acid $\rightarrow$
3. Magnesium + silver nitrate solution $\rightarrow$
4. Sodium + water $\longrightarrow$

D. Double Displacement

1. Solutions of ammonium sulphate + barium chloride $\longrightarrow$
2. Solutions of aluminium sulphate + potassium hydroxide $\longrightarrow$
3. H_2S gas is bubbled through copper (II) chloride solution.
4. Sulphuric acid + calcium hydroxide solution $\longrightarrow$

- 5-4 Give definition for oxidation and reduction in terms of loss and gain of electrons.
- 5-5 What is meant by oxidizing and reducing agents? Give illustrations of each.
- 5-6 Label the following changes as oxidation or reduction:
- $\text{Al}^{3+} \rightarrow \text{Al}$
 - $\text{Au} \rightarrow \text{AuCl}_3$
 - $\text{Br}^- \rightarrow \text{Br}_2$
 - $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
- 5-7 Define anode and cathode in terms of oxidation and reduction.
- 5-8 Give three examples of exothermic and three examples of endothermic reactions.
- 5-9 Explain how and why the following factors affect the rate of a reaction?
- An increase in concentration
 - A rise in temperature
 - The addition of a catalyst.
- 5-10 What is a catalyst?
- 5-11 During a chemical reaction, what happens to a catalyst?
- 5-12 In the following reactions, indicate whether an increase or decrease of pressure will favour the forward reaction:
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
 - $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$
 - $\text{CuO}(\text{s}) + \text{H}_2(\text{g}) \rightleftharpoons \text{Cu}(\text{s}) + \text{H}_2\text{O}(\text{l})$
 - $\text{COCl}_2(\text{g}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{CO}(\text{g})$
- 5-13 What effect would heating have on the following reactions?
- $\text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2\text{CO} - \text{heat}$
 - $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) - \text{heat}$
 - $(\text{NH}_4)_2\text{CO}_3(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) - \text{heat}$
 - $\text{PCl}_3(\text{s}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g}) + \text{heat}$
- 5-14 A solution containing I^- is added to a solution containing Fe^{3+} . Fe^{2+} and I_2 are produced. Give the balanced equation. What is oxidized and what is reduced?
- 5-15 How will you explain the evolution and absorption of heat in a chemical reaction?
- 5-16 Explain what is meant by the statement that a chemical equilibrium or a physical equilibrium is a dynamic equilibrium.
- 5-17 Describe an experiment to distinguish between an electrolyte and a non-electrolyte.
- 5-18 Discuss the importance of pH in agriculture and in biological processes.
- 5-19 Two solutions A and B have pH values of 3.0 and 9.5 respectively. Which of these will turn blue litmus red and which will turn red litmus blue.
- 5-20 Four solutions A, B, C, and D have pH values 2.5, 5.4, 8.3 and 10.5 respectively.
- Which of these is most acidic and which is most basic?
 - Arrange them in order of decreasing $[\text{H}^+]$.
- 5-21 Give the names and formulae of the three most important strong acids.
- 5-22 Define pH and pOH by writing in mathematical equation for each.
- 5-23 Calculate
- The pH of a solution whose $\text{pOH}=6$
 - The pH of a solution whose $\text{pOH}=14$
 - The pH of a solution whose $\text{pOH}=1$
- [Ans. (a) 8, (b) 0, (c) 13]
- 5-24 Calculate the pH of the following solutions:
- 10^{-6} M HCl
 - 10^{-9} M NaOH
 - 10^{-5} M HCl
 - 10^{-3} M HCl
- [Ans. (a) 6, (b) 5, (c) 5, (d) 3]
- 5-25 Calculate the $[\text{H}^+]$ in the following solutions:
- $\text{pOH}=12$
 - $\text{pH}=6$
 - $\text{pH}=4$
 - $\text{pOH}=8$
- [Ans. (a) 10^{-2} M , (b) 10^{-6} M , (c) 10^{-4} M , (d) 10^{-6} M]

UNIT 6

Non-Metals



Antoine L. Lavoisier
(1743—1794)

Antoine L. Lavoisier, a French scientist, is called the 'Father of Modern Chemistry'. He founded the correct theory of combustion. His name is associated with the discovery of some of the elements and some phenomena in chemistry.

Learning Objectives

At the completion of this unit, you should be able to :

1. Differentiate between metals and non-metals with reference to their physical and chemical characteristics.
2. Classify the oxides—acidic, basic or neutral—of metals and non-metals on the basis of their reaction with water.
3. Characterize the non-metals on the basis of their chemical properties, *e.g.*, reaction with acids, etc.
4. Discuss and appreciate the unique position of hydrogen in the periodic table.
5. Understand the concept of allotropy seen among various non-metals.
6. Give reasons for the inert nature of noble gases and extremely reactive behaviour of halogens lying close to them.
7. Account for the source of various non-metals in the native and combined forms.
8. Explain the atomicity of various non-metals.
9. Understand the nature of bonding in compounds described in this unit.
10. Prepare the gases listed in the unit and study their important properties.
11. Explain the working principle of Kipp's apparatus employed for the preparation of H_2S gas.
12. Demonstrate some of the reactions of the compounds described in this unit.
13. Emphasize the importance of hydrogen sulphide for qualitative inorganic analysis.
14. Differentiate between the bleaching action of sulphur dioxide and chlorine.

15. Explain the principle of contact process for the manufacture of sulphuric acid.
16. Demonstrate the dehydrating properties of sulphuric acid.
17. Prepare a dilute solution of sulphuric acid.
18. Demonstrate certain reactions of sulphuric acid on metals, e.g., copper, zinc, etc.
19. Give reasons for the inertness of nitrogen.
20. Demonstrate the fountain experiment.
21. Explain the principle involved in the manufacture of NH_3 gas by Haber's process and nitric acid by Ostwald's process.
22. Demonstrate the reaction of nitric acid on metals and non-metals
23. Demonstrate the brown-ring test for detecting NO_3^- ion.
24. Differentiate between chlorides, bromides and iodides.
25. Prepare a solution of hydrogen chloride in water.

6-1 INTRODUCTION

Elements, based upon their physical and chemical characteristics and nature of their compounds, are divided in three groups: metals, non-metals and metalloids. With the exception of hydrogen, non-metals are located in the upper right hand region of the periodic table. They have their own characteristic properties and show chemical diversity in their chemical reactions. They include both inert non-metals, e.g., He, Ne, Ar, Kr, Xe and extremely reactive non-metals like F, Cl, Br, I. In between these two extremes, we have non-metals of intermediate reactivities, e.g., N, P, O and S.

The general properties that distinguish between metals and non-metals are summarized in Tables 6-1 and 6-2.

Table 6-1 Physical properties of metals and non-metals

Metals	Non-metals
1. High electrical conductivity	Hardly conduct electricity (Graphite, an allotrope of carbon is an excellent conductor of electricity)
2. High thermal conductivity	Good heat insulators
3. High density	Low density
4. Possess lustre	Do not possess any metallic lustre (iodine has shining crystals).
5. Generally solids (mercury is liquid)	Solids (C, S, Se, P, I) Liquids (Br) Gases (O, N, F, Cl)
6. Ductile (can be drawn into wires)	Non-ductile
7. Malleable (can be hammered into sheets)	Brittle in solid state
8. Solid state characterized by metallic bonding	Covalently bonded molecules; inert gases are monoatomic

Table 6-2 Chemical properties of metals and non-metals

Metals	Non-metals
1. Valence shell contains a few electrons; usually three or four	Valence shell contains four or more electrons
2. Electropositive	Electronegative
3. Reducing agents	Oxidizing agents
4. Form cations by losing electrons	Form anions by gaining electrons
5. Form basic oxides which on hydrolysis give hydroxides	Form acidic oxides which on hydrolysis give acids

The position of metals, non-metals and metalloids is shown below in the periodic table (Fig. 6-1). Hydrogen occupies a unique position in the periodic table.

Among the non-metals some very striking differences in physical properties are found. Carbon, for example, is almost impossible to melt and nitrogen is extremely difficult to liquefy. Often a single element can exist in more than one forms. Phosphorus and sulphur exist in number of forms. These forms are called allotropes and the property is called allotropy. These allotropic forms of one element differ in reactivity.

The non-metals and their compounds play a vital role in chemistry and in our lives. Hydrogen and oxygen react with each other to form H_2O (water), a simple molecule, whose unusual properties are necessary for the development and maintenance of life. Sugar (or carbohydrates), an important sources of energy, contains C, H and O. Proteins, the body-building materials, contain C, H, O and N as their constituents. Detergents, vitamins, fertilizers, medicines, etc., all contain some of the non-metals.

H		← NON-METAL						He
Li	Be	B	C	N	O	F	Ne	
Na	Mg	Al	Si	P	S	Cl	Ar	
K	Ca	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	In	Sn	Sb	Te	I	Xe	
Cs	Ba	Tl	Pb	Bi			Rn	

↑ METALS ↑ TRANSITION ELEMENTS ↑ METALS ↑ BRIDGING ELEMENTS BETWEEN ELECTROPOSITIVE AND ELECTRONEGATIVE ELEMENTS (METALLOIDS) ↑ NON-METALS

PARTIAL SHADING OF Ga, Sn, As AND Te EXHIBITS SOME PERCENTAGE OF METALLOIDIC BEHAVIOUR

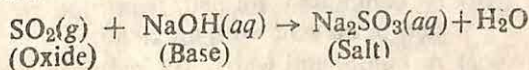
Fig. 6-1 Metals, non-metals and metalloids in the periodic table

6-2 GENERAL CHARACTERISTICS OF NON-METALS AND METALS

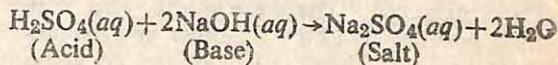
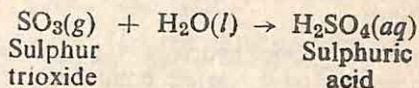
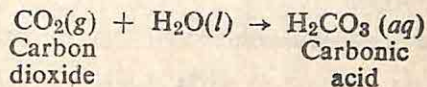
Some of the characteristic properties of non-metals have already been listed in Tables 6-1 and 6-2. Some other properties in which non-metals differ from metals are discussed below :

6-2-1 OXIDES

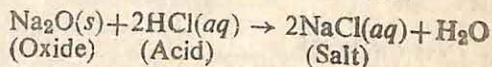
Non-metals form covalent oxides which are either acidic or neutral. Many oxides are vapours or liquids at room temperature. These oxides react with a base to form a salt and water.



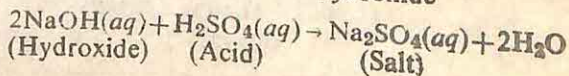
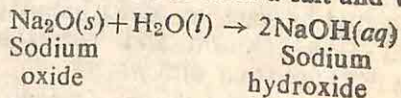
Most of the acidic oxides react with water to form the corresponding oxyacid. Acidic oxides may therefore be regarded as derived from acids by eliminating water; hence, they are also known as acid anhydrides. The acid itself also reacts with a base to form a salt and water.



Metals form ionic oxides which are basic in nature. Most of the oxides are solids with high melting and boiling points. They react with an acid to form a salt and water.



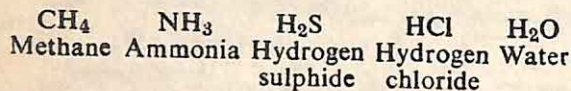
Also, the basic oxide reacts with water forming a hydroxide. The hydroxide itself also reacts with an acid to form a salt and water.



Experiment 6-1 To study the acidic nature of the product formed by the reaction of oxide with water. Take the product say dilute H_2SO_4 in a test tube. Insert a piece of blue litmus paper into test tube so that it touches the liquid in the test tube. The blue paper turns red. This shows the acidic nature of the liquid. Repeat this experiment with other acids and observe the colour change.

6-2-2 HYDRIDES

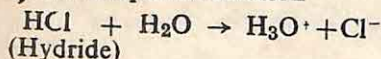
Non-metals form covalent hydrides on combining with hydrogen under different conditions. For example,



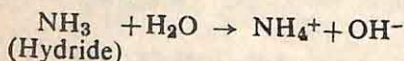
Most of the hydrides are gaseous in nature. They are stable and not hydrolyzed by water. They dissolve to a greater or lesser extent in water to give solutions which may be acidic, basic or neutral according to whether the hydride in aqueous solution can donate a proton, accept a proton or do neither.

Examples

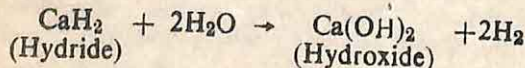
Acidic in aqueous solution



Basic in aqueous solution

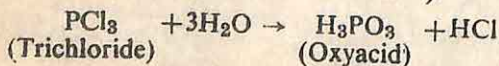


Metals form ionic hydrides on combining with hydrogen under varied conditions, e.g., CaH_2 , MgH_2 , etc. These are solids with high melting points. They are unstable and decompose on heating. They are hydrolyzed by water forming the hydroxide of the metal and hydrogen.



6-2-3 CHLORIDES

Non-metals on combining with chlorine gas form covalent chlorides, e.g., HCl , CCl_4 , etc. They are volatile in nature. They are irreversibly hydrolyzed by water to give a solution of the oxyacid of the element and hydrochloric acid (CCl_4 does not react with water).

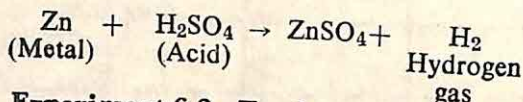


Metals on combining with chlorine gas form ionic chlorides, e.g., NaCl , BaCl_2 , etc. They are solids with high melting points. They are stable and dissolve in water to give solutions. Aqueous solution contains ions.

6-2-4 REACTION WITH ACIDS

Non-metals do not react with acids like dilute HCl , dilute H_2SO_4 , etc., and hence, do not replace hydrogen from acids.

Metals react with acids producing hydrogen gas.



Experiment 6-2 To demonstrate that non-metals do not react with dilute acids. Take dilute sulphuric acid in three test tubes numbered as 1, 2, 3. Introduce a small amount of sulphur into the test tube-1, a piece of white phosphorus into the test tube-2 and a small amount of powdered carbon into the test tube-3. Now it is observed that no reaction takes place in any of the test tubes and the hydrogen gas is not evolved. Repeat the experiment by taking dilute HCl .

WORK EXERCISES

1. Make a list of the metals and non-metals with which you have been familiar since childhood.
2. State some of the properties of non-metals which are not common to metals.
3. Indicate the positions of the metals, non-metals and metalloids in the periodic table.
4. Write the electronic arrangements of the non-metals which you propose to study in this unit.
5. What is the term assigned to the following :
 - (i) Elements along the border between the true metals and non-metals.
 - (ii) A binary compound in which hydrogen is one of the elements.
 - (iii) A compound formed from the reaction of an acid with an alkali.
 - (iii) A compound which on reducing with water gives an acid.
6. Name the following :
 - (i) A non-metal which is liquid at room temperature.
 - (ii) A metal which is liquid at room temperature.

(iii) A non-metal which melts at very high temperature.

(iv) One non-metal from the groups, IA, IVA, VA, VIA and VIIA.

(v) The nature of bond usually non-metals form with each other.

7. Give two examples of each of hydrides, chlorides and oxides of non-metals with their electron dot structures.

8. What happens when :

(i) SO_3 is dissolved in water.

(ii) PCl_3 is attacked by water.

(iii) Zinc reacts with dilute sulphuric acid.

(iv) SO_2 is passed through the solution of sodium hydroxide.

Give chemical equations.

9. What happens when oxides of non-metals are dissolved in water ? Illustrate.

10. (i) Define an acidic oxide.

(ii) How will you establish that SO_2 is an acidic oxide ?

HYDROGEN

(Group IA Non-metal)

6-3. HYDROGEN

Symbol	H	Relative atomic mass	1.008
Molecular formula	H_2	Relative molecular mass	2.016
		Atomic number	1

Hydrogen was discovered in 1776 by Henry Cavendish by the action of dilute sulphuric acid on iron. He investigated its properties and showed that water is the only product when hydrogen burns in air. It was because of this reaction that the 'inflammable air' as called by Cavendish was named hydrogen (Greek, *hydro* genon meaning water former) by Lavoisier.

Hydrogen is the first element in the periodic table. It is the lightest element. An atom of hydrogen has one proton and one electron.

Place in the periodic table

It occupies a unique position in the periodic table. In its properties, it behaves like alkali metals (IA group) as well as like halogens (VIIA group). Hydrogen, thus, finds its assignment both with alkali metals and halogens. It can lose its only electron to form H^+ ion, and thus it resembles alkali metals (M) which yield M^+ ions. It can also form H^- ion by gaining one electron similar to halogens (X) forming X^- ions. In its atomicity, it also resembles halogens (both halogens and hydrogen exist in diatomic form).

Hydrogen can also form a single covalent bond with other atoms like C, Si, etc. Therefore, hydrogen can be considered as a non-metal in respect of some of its properties.

Isotopes of hydrogen

Three isotopes of hydrogen are known (Table 6-3).

They show different physical properties due to large mass difference. This can be confirmed by comparing the properties of H_2O and D_2O (heavy water). Heavy water has higher density, freezing point and boiling point than water. Heavy water is used as a moderator in nuclear reactors to regulate the speed of fast moving neutrons.

6-3-1. OCCURRENCE

Hydrogen, because of its reactivity is rarely found in the free state at the earth's surface though it is present in the Sun and in interstellar space (in isolated form, H(g)). It does not occur in the atmosphere except in trace quantities.

However, in the combined form, it constitutes about 1 percent of the crust of the earth. The most important compound of hydrogen is

Table 6-3. Characteristics of isotopes of hydrogen

Isotope	Notation	Electron	Proton	Neutron	Relative atomic mass
Hydrogen-1 (Protium)	${}^1_1\text{H}$	1	1	0	1
Hydrogen-2 (Deuterium)	D or ${}^2_1\text{H}$	1	1	1	2
Hydrogen-3 (Tritium)	T or ${}^3_1\text{H}$	1	1	2	3

water which contains 11 percent by weight of hydrogen. Hydrogen is present in all acids and bases. It is a constituent of carbohydrates, proteins, fats and oils. Most of the fuels such as wood, coal, coke, cooking gas, petrol, etc. also contain hydrogen as a major constituent.

6-3-2. PREPARATION OF HYDROGEN

Hydrogen is prepared in the laboratory by the action of dilute H_2SO_4 or HCl on granulated zinc (metal placed above hydrogen in the electrochemical series). The gas is collected by the downward displacement of water. The apparatus employed is portrayed in Fig. 6-2.

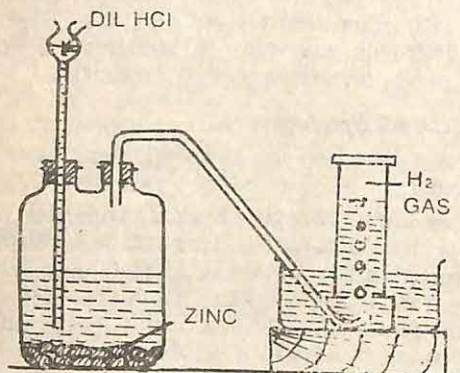
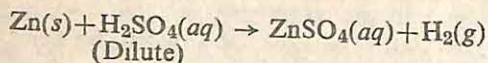


Fig. 6-2. Laboratory preparation of hydrogen

To remove any trace of acid the gas is bubbled through KOH solution. Hydrogen can be dried by passing through concentrated sulphuric acid or phosphorous pentoxide (Fig. 6-3).

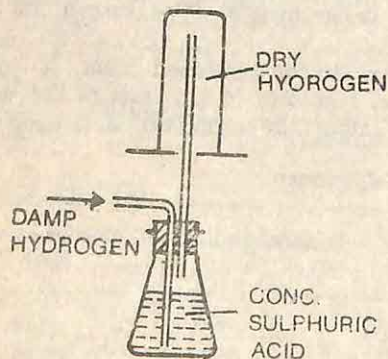
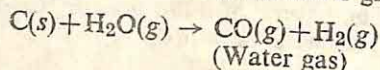


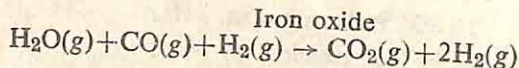
Fig. 6-3. Drying of hydrogen gas

Hydrogen is produced by the electrolysis of acidified water. It is also a byproduct of com-

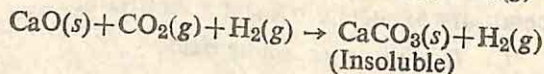
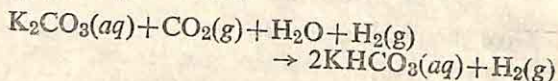
mercial preparation of chlorine and sodium hydroxide by electrolysis of brine (sodium chloride solution). Hydrogen is also manufactured from water gas (Bosch's process). Steam is passed through very hot coke, the gaseous products are known as water gas.



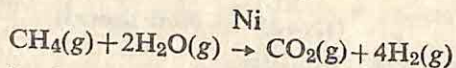
Water gas is then passed, with excess steam, over a heated iron (III) oxide catalyst. The carbon monoxide then reacts with the steam to form more hydrogen.



Carbon dioxide is removed by bubbling gases through hot K_2CO_3 solution under pressure or by passing over lime.



Large amounts of hydrogen are now produced by passing steam and petroleum gases (hydrocarbons) over a nickel catalyst.



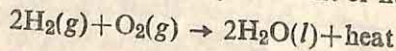
Carbon dioxide can be removed by either of the above methods.

6-3-3. PROPERTIES OF HYDROGEN

Hydrogen is a colourless, odourless and tasteless gas which is almost insoluble in water and is liquefied only with great difficulty. It is the lightest known gas. Its density is 0.071 g/cm^3 . Its melting point is 14K and boiling point is 19.3K .

Hydrogen does not show any reaction with litmus, and hence, it is neither acidic nor basic.

Hydrogen burns in air (or oxygen) with a blue flame (highly inflammable) producing water (Fig. 6-4). The reaction is accompanied with the evolution of large amount of heat.



Hydrogen does not support burning.

1. **Reaction with non-metals:** Hydrogen combines with non-metals forming hydrides. It combines with chlorine in the bright

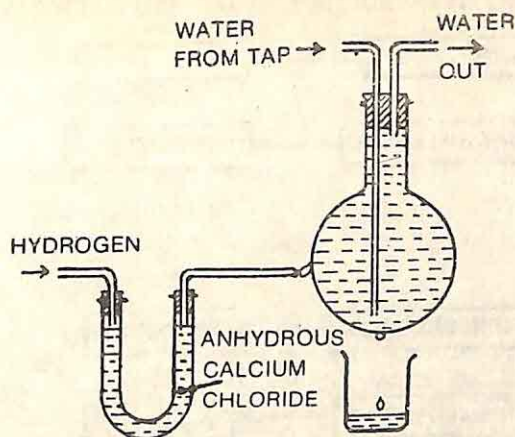
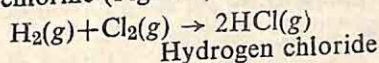


Fig. 6-4. Burning of dry hydrogen in air to form water

sunlight or when its burning flame comes in the contact of chlorine (Fig. 6-5).



Bromine and iodine combine only on heating. It also combines with nitrogen in the presence of a catalyst under suitable conditions of temperature and pressure forming ammonia (Haber's process).

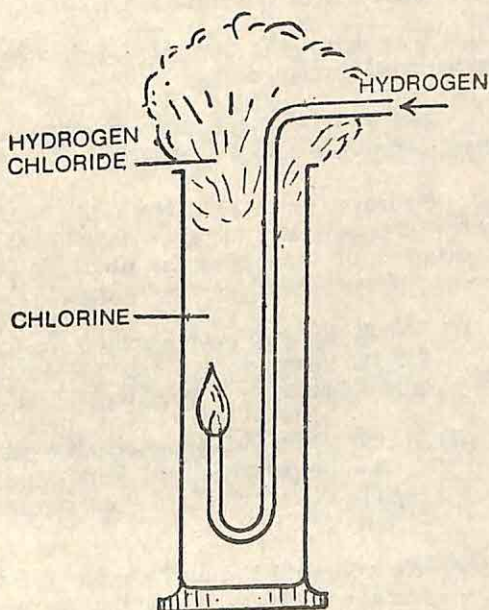
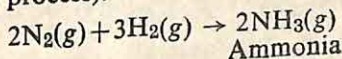
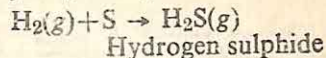
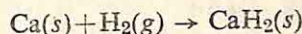
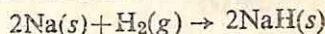


Fig. 6-5. A hydrogen flame in a jar of chlorine gas

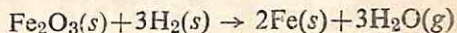
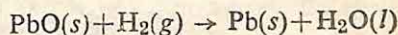
Hydrogen, on passing through boiling sulphur, forms hydrogen sulphide.



2. **Reaction with metals :** Hydrogen combines with active metals forming hydrides.



3. **Reaction with compounds :** Hydrogen acts as a reducing agent. It reduces metal oxides (oxides of metals present below hydrogen in the electrochemical series) to their metallic forms.



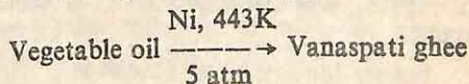
6-3-4. USES OF HYDROGEN

1. Hydrogen was used earlier in filling balloons and airships. However, on account of its highly inflammable nature, it has now been replaced by helium. It is still used in meteorological and cosmic research balloons because of its extremely low density.

2. It is used in the manufacture of ammonia (by Haber's process) which is the basis of many fertilizers. Fertilizers are used extensively to yield better crops.

The major bulk of commercially produced hydrogen is used in producing hydrochloric acid, explosives, plastics and a large number of organic chemicals. (Fig. 6-6).

3. It is used in the manufacture of *vanaspati ghee*. This process is called hydrogenation or hardening of oils. The hydrogenated products have superior keeping qualities.



4. Hydrogen is used in the manufacture of petrol. This is done by hydrogenation of powdered coal or coke at a moderately high temperature and under very high pressure.

5. The high heat of combustion of hydrogen makes it valuable as a fuel. It is used as a fuel mixed with other gases in coal gas and water gas. Hydrogen is carried by the rocket as a liquid at very low temperature and is burnt in the rocket motor with oxygen. Liquid

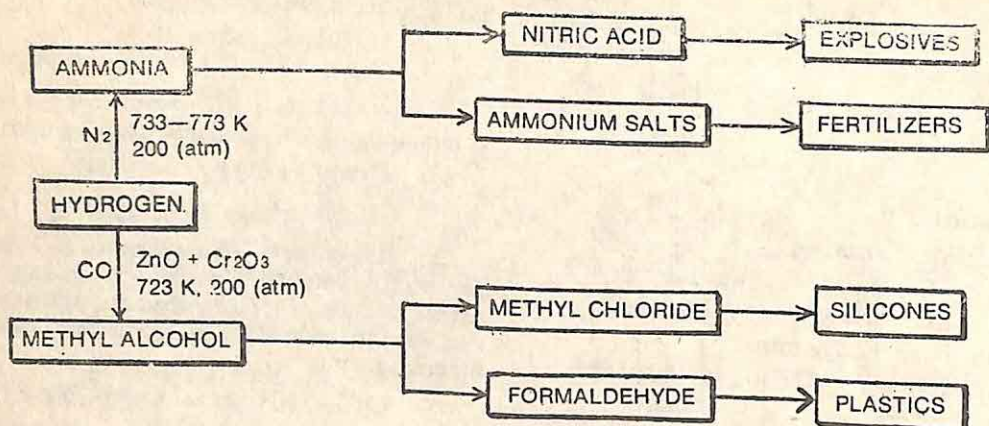
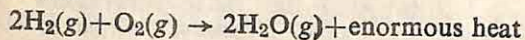


Fig. 6-6. Flow sheet illustrating uses of hydrogen

hydrogen is likely to be developed as fuel for motor vehicle in future.

6. Oxy-hydrogen flames which have a temperature of about 2273K are used for welding and cutting metals. The flames are also used for fusing alumina to produce rubies and sapphires used as bearings (jewels) in watches.



7. It is used as a reducing agent in certain metallurgical operations.

WORK EXERCISES

1. List important sources of hydrogen.
2. Account for the fact that hydrogen is present in minute amounts in the atmosphere.
3. State two methods of preparing hydrogen.
4. Hydrogen is not found free in nature. Comment.
5. Answer the following questions :
 - (i) Can hydrogen burn ?
 - (ii) Is hydrogen lighter or heavier than air ?
 - (iii) Does heavy water boil at higher temperature than water ?
 - (iv) Can hydrogen be produced by the electrolysis of water ?
 - (v) Is hydrogen acidic or basic ?

(vi) Can hydrogen support combustion ?

(vii) Is reduction a chemical process in which hydrogen is removed from a compound ?

(viii) Can hydrogen be used as a fuel ?

6. What is water gas ? How is it prepared ?

7. What is hydrogenation ?

8. Why have the isotopes of hydrogen been assigned special names ?

9. Name one element more reactive and another less reactive than hydrogen.

10. Hydrogen gas is prepared in the laboratory by the action of a metal on an acid. Give the diagram of the apparatus used for the purpose. Answer the following questions ?

- (i) Which of the following metals is used for the purpose and why ? copper, zinc, magnesium or sodium.
- (ii) Which of the following acids is used in the preparation and why ? dilute H_2SO_4 , dilute HNO_3 or concentrated HNO_3 .
- (iii) It is necessary to run the apparatus for sometime before collecting the gas. Why ?

NITROGEN AND PHOSPHORUS

(Group VA Non-metals)

6-4 NITROGEN

Symbol	N
Relative atomic mass	14
Molecular formula	N ₂
Relative molecular mass	28
Atomic number	7

Nitrogen was probably first recognized as a distinct gas by Rutherford in 1772. Lavoisier, later recognized its elemental nature on the basis of his work on combustion. He called the gas azote (Greek, a zoe=not life) as it would not support life. But its name nitrogen was preferred because of its close relationship to nitre (Greek, nitron genon=nitre former).

Nitrogen is very much essential for all living organisms. Nitrogen present in the air dilutes oxygen and brings down its activity to safe limits. Nitrogen, in the combined form as proteins, is needed by plants and animals for the life process. It cannot be directly assimilated in the free state. The process of converting free atmospheric nitrogen into its useful compounds is called fixation of nitrogen.

Place in the periodic table and general characteristics. Nitrogen is a typical non-metal. It belongs to group VA of the periodic table. Its electronic configuration is 2, 5 with five electrons in the valence shell. It is a diatomic molecule. It exists as discrete diatomic molecules in the gaseous, liquid and solid states. Two nitrogen atoms are combined by triple bonds.



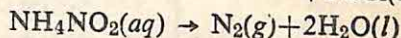
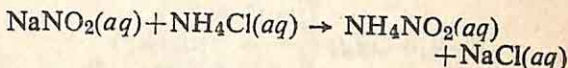
6-6-1 OCCURRENCE

Nitrogen occurs abundantly in the nature in the free as well as in the combined forms. Elemental nitrogen makes up 78% (by volume) of the atmosphere. It is obtained from the atmosphere by liquefaction and fractionation. It is present in certain solid nitrate deposits, notably as NaNO₃, in the earth's crust. Nitrogen is present in the amino acids from which animal and vegetable proteins are constructed. It also occurs in traces as ammonia in the atmosphere and is produced by the decay of organic matter and urine. In plants, animals,

rock salts and mineral waters nitrogen exists in the form of ammonium salts.

6-6-2 PREPARATION OF NITROGEN

Commercially nitrogen is obtained by the fractional distillation of liquid air. In the laboratory, nitrogen is produced by heating an equimolecular solution of sodium nitrite and ammonium chloride. These interact to give ammonium nitrite, which then decomposes to give nitrogen. The gas is collected over water :



The assembly employed for the preparation of nitrogen is given in Fig. 6-7.

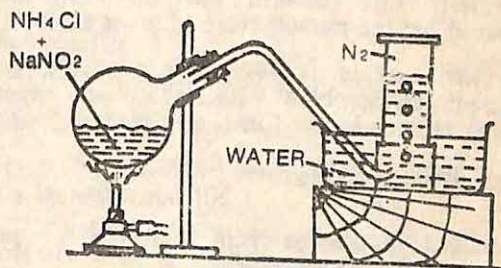


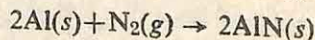
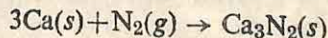
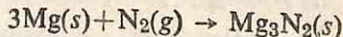
Fig. 6-7. Preparation of nitrogen

6-6-3 PROPERTIES OF NITROGEN

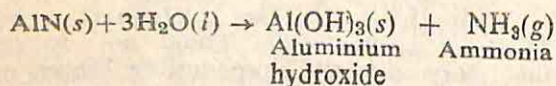
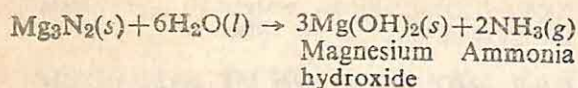
Nitrogen is a colourless and odourless gas. It is lighter than air and almost insoluble in water. It is liquefied only with difficulty. Its melting point is 63.2K and boiling point is 77.2K. Its density is 0.879 g/cm³. It is neutral towards litmus.

Nitrogen is very stable and relatively inert. It is neither combustible nor a supporter of combustion. Combustion reactions are slowed down by the presence of nitrogen in air. It dilutes the effect of oxygen in air.

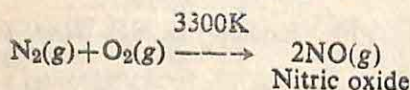
1. Reaction with metals. Nitrogen, however, combines with some heated metals to form nitrides which are white solids.



Nitrides decompose on reacting with water producing metal hydroxide and ammonia gas with characteristic pungent odour.

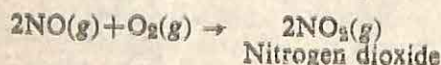


2. Reaction with oxygen. Nitrogen combines with oxygen at 3300K to form nitric oxide in very small yield. Such high temperatures are produced by electric sparks.



Atmospheric nitrogen and oxygen also undergo this reaction during lightning. The reaction is reversible and is highly endothermic. Formerly this reaction was the basis of a method for the manufacture of nitric acid.

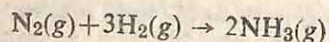
Nitric oxide is thermally unstable and immediately combines with atmospheric oxygen giving reddish brown fumes of nitrogen dioxide.



Nitrogen dioxide gets dissolved in rain water producing nitric acid.



3. Reaction with hydrogen. Nitrogen combines with hydrogen to give ammonia. The reaction takes place at 750K under high pressure in the presence of finely divided iron catalyst.



The reaction is reversible and exothermic. This reaction is the basis of Haber's process for the manufacture of ammonia.

6-6-4 USES OF NITROGEN

1. The important uses of nitrogen are based upon its inactivity. It is used :

(i) For providing inert atmosphere in chemical processes.

(ii) To prevent the oxidation of easily oxidizable substances on exposure to air.

(iii) For providing inert atmosphere in industries while handling gasoline and other inflammable liquids.

(iv) In mercury thermometers for filling the space above mercury and thus reducing the evaporation of mercury.

(v) In the packing of foods. Canned foods such as coffee, hydrogenated vegetable oils etc. retain their flavour and colour much better if packed in the atmosphere of nitrogen instead of air.

(vi) For filling in electric bulbs.

2. Nitrogen is used in various processes for 'fixing' atmospheric nitrogen.

3. It is used in the manufacture of nitro-lime, ammonia, nitric acid and fertilizers.

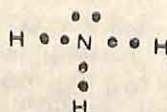
4. Liquid nitrogen is used as a coolant when low temperatures are required.

6-6-5 COMPOUNDS OF NITROGEN

Ammonia and nitric acid are amongst the important industrial chemicals. Their chemistry is discussed in the following pages.

6-7 AMMONIA

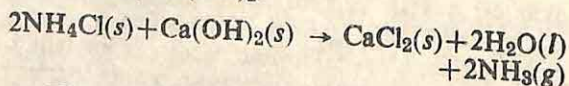
Molecular formula	NH_3
Relative molecular mass	17
Electron dot structure	



Ammonia is a very important compound for the fertilizer industry. It is present in atmosphere. Decaying of organic matter, e.g., horns and hoofs of dead animals and dead plants, produces ammonia gas. It occurs in nature as ammonium chloride and ammonium sulphate which are found in some springs and earth's crust. The smell around toilets is also due to this gas.

6-7-1 LABORATORY PREPARATION OF AMMONIA

Ammonia is prepared in the laboratory by heating a mixture of ammonium chloride and slaked lime, $\text{Ca}(\text{OH})_2$.



The apparatus used in the preparation of the gas is portrayed in Fig. 6-8. A finely ground mixture of ammonium chloride (1 part) and slaked lime (2 parts) is placed in a round

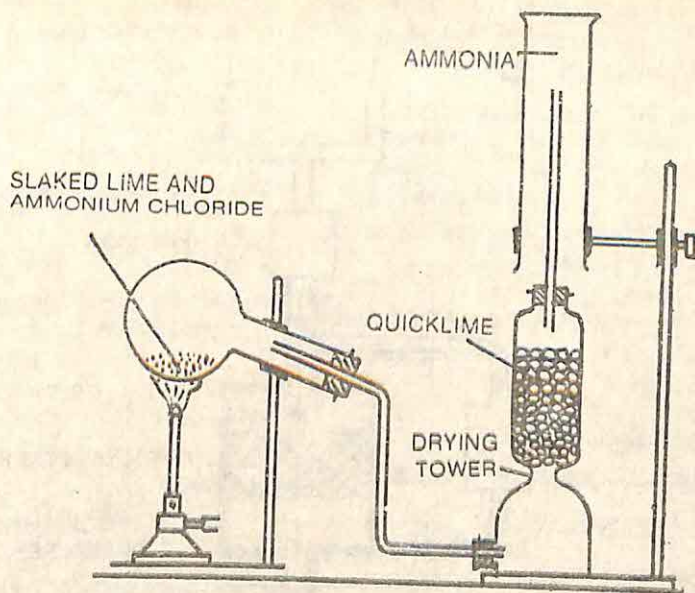
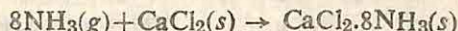
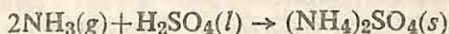


Fig. 6-8. Laboratory preparation of ammonia

bottom flask. On heating, ammonia is evolved. The gas is passed through quicklime (for drying) and collected by the downward displacement of air as it is lighter than air. It cannot be collected over water because it is highly soluble in water. Water is formed during the course of reaction. The flask is always positioned in a tilted fashion to avoid the condensed water drops which may trickle back on to the hot glass and crack it.

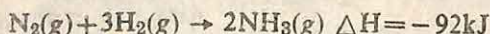
Both sulphuric acid and anhydrous calcium chloride cannot be used for drying as both react with ammonia.



A hard glass boiling tube can also be used in place of round bottom flask.

6-7-2 MANUFACTURE OF AMMONIA

Ammonia is manufactured synthetically by the direct combination of nitrogen and hydrogen under suitable conditions. This reaction was discovered by a German chemist, Fritz Haber in 1908 and is called the Haber's process :



Nitrogen is obtained by fractional distillation of liquid air and hydrogen is obtained from natural gas or by the Bosch's process. The

two gases are dried and mixed in the ratio of 1 : 3 by volume.

The reaction is reversible, exothermic and proceeds with a decrease in volume. Hence, according to Le Chatelier's principle, high pressures and low temperatures should give better yield. At low temperatures, however, chemical reactions proceed slowly. In practice, an optimum temperature of 773K and a pressure of 250—1000 atm are employed. A mixture of two gases compressed to 250—1000 atm is passed over finely divided iron (catalyst) heated to 773K. Alumina or molybdenum is added to act as promotor. The products are passed through a cooling chamber (Fig. 6-9). Under the high pressure the ammonia then liquefies and can be separated.

6-7-3 PROPERTIES OF AMMONIA

Ammonia is a colourless gas with a characteristic choking smell. It is lighter than air. It is highly soluble in water. It can be easily liquefied to a colourless liquid (b.p. 240K).

Fountain experiment to show the solubility of ammonia in water and its alkaline nature. A round bottomed flask is taken and is fitted with a rubber cork through which a glass jet passes (Fig. 6-10). A glass dropper also passes through the rubber cork. The flask is filled with ammonia gas. The flask with the glass jet and the dropper is placed

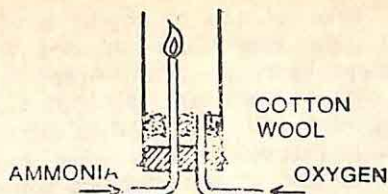
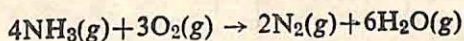
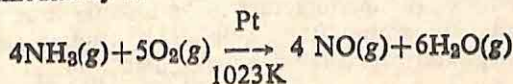


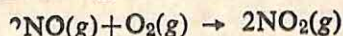
Fig. 6-11. Burning of ammonia with a green flame in an atmosphere of oxygen



In the presence of heated platinum catalyst, the ammonia is oxidized to nitric oxide, which immediately combines

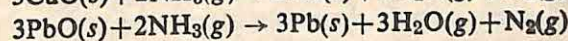
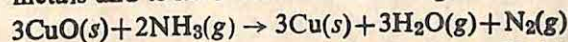


with atmospheric oxygen to give brown coloured nitrogen dioxide gas.

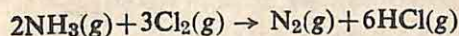


This reaction is used in the manufacture of nitric acid from ammonia.

3. Reducing properties. (i) Ammonia reduces heated metallic oxides of less reactive metals and is itself oxidized to nitrogen.



(ii) It reduces chlorine to give hydrogen chloride.

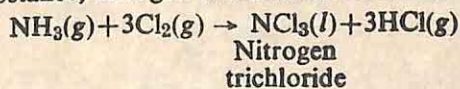


(When the end of the delivery tube from which ammonia gas is coming is lowered into a gas jar full of chlorine, the ammonia gas ignites spontaneously and is oxidized to nitrogen).

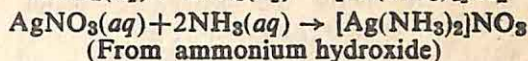
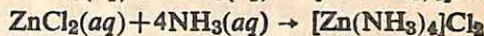
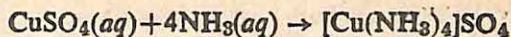
The hydrogen chloride thus formed combines with excess of ammonia producing dense white fumes of ammonium chloride.



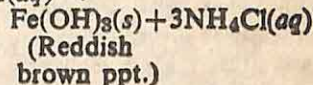
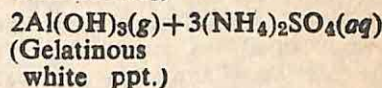
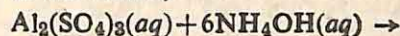
If excess of Cl_2 is used, a highly explosive substance, nitrogen trichloride is formed.



4. Complex formation. On adding ammonia or ammonium hydroxide solution to salt solutions of metals such as Cu, Zn and Ag, complex compounds are formed.



5. Formation of hydroxides. With solutions of salts of some metals, ammonium hydroxide causes precipitation of hydroxides of the metals,



6-7-4 TEST FOR AMMONIA GAS

NH_3 can be recognized by its characteristic choking smell.

When a glass rod dipped in concentrated hydrochloric acid is brought near the mouth of a gas jar containing ammonia gas, dense white fumes of ammonium chloride are formed.

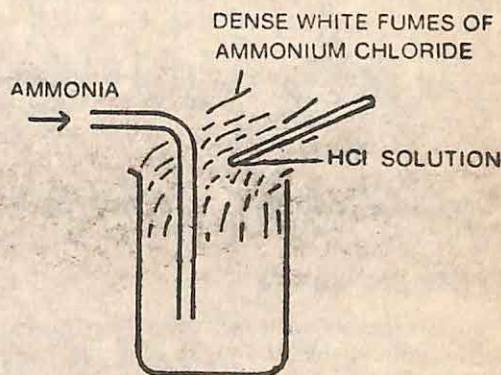
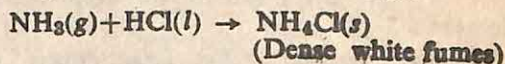


Fig. 6-12 Identification of ammonia gas



6-7-5 PREPARATION OF AN AQUEOUS SOLUTION OF AMMONIA

When ammonia combines with water, ammonium hydroxide is formed.



A concentrated solution cannot be prepared by just passing ammonia gas through a tube into water, since the high solubility of ammonia would cause the water to flow back into the generating vessel. Hence a simple device to

prevent sucking back is used as shown in Fig. 6-13. The wide opening of the funnel is allowed to be below the surface of water. When water begins to suck back, the level of the water in the beaker becomes lower, and consequently the contact between the funnel and the water surface is disturbed. Air then enters the funnel and the water falls into the beaker. The process is repeated until a saturated solution is obtained. Then the ammonia just bubbles through its concentrated solution. A solution of ammonium hydroxide always smells of ammonia. This is because the reaction of ammonia with water is reversible. Generally ammonia is obtained in the laboratory by warming the concentrated solution of ammonium hydroxide solution in a flask fitted with a delivery tube. The decomposition is accelerated by heat and also by blowing air through the solution.

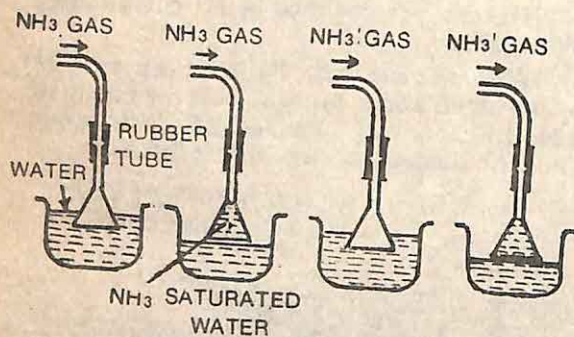


Fig. 6-13 A simple device to prevent sucking back in the preparation of aqueous solution of ammonia

6-7-6 EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers.

1. To prepare a sample of ammonia gas (Section 6-7-1)
2. To identify the ammonia gas (Section 6-7-4)
3. To prepare an aqueous solution of ammonia (Section 6-7-5)
4. To show the basic nature of the ammonia gas and its aqueous solution (Section 6-7-3)
5. To demonstrate the fountain experiment (Section 6-7-3)
6. To prepare the solution of cupric tetra-ammine sulphate.

Hint: Take solution of copper sulphate in a beaker. Add concentrated solution (1 : 1) of ammonium hydroxide with stirring. To start with a pale blue copper (II) hydroxide is precipitated which will dissolve, if an excess of ammonium hydroxide is present, to give a deep blue solution of tetra-ammine complex of Cu (II).

7. To observe some other physical and chemical properties alkaline nature, reaction with oxygen, chlorine, etc. (Section 6-7-3).

6-7-7 USES OF AMMONIA

Ammonia is used :

1. In the manufacture of various fertilizers, such as ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, etc.
2. In the manufacture of nitric acid (Ostwald's process), sodium cyanide, ammonium chloride (used in dry cells, Leclanche cells and preparing digestive medicines), ammonium nitrate (used in making explosives and in the manufacture of calcium ammonium nitrate, CAN), ammonium carbonate (used in baking powders), etc. .
3. In Solvay's process for the manufacture of sodium carbonate and sodium bicarbonate.
4. In the manufacture of polyamide plastics and many organic chemicals and wood pulp.
5. In the manufacture of artificial silk (rayon).
6. As a refrigerating agent in ice-plants.
7. Ammonia-water solution is used for removing grease stains. The solution is also used for cleaning window panes, porcelain tiles, etc.
8. In household detergents.
9. Liquid ammonia is used as a non-aqueous solvent.
10. Alkali metal-ammonia solution is used for reduction purposes in organic reactions.

6-8 NITRIC ACID

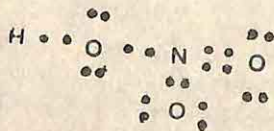
Molecular formula

Relative molecular mass

Electron-dot structure

HNO_3

63



Nitric acid was known as 'aqua fortis' (strong water) to the early alchemists because of its corrosive action on many substances. In 1658, Glauber prepared it using sulphuric acid and potassium nitrate (a present laboratory method). Traces of free nitric acid are found in rain water after thunderstorm and lightning. Lightning initiates the combination of atmospheric nitrogen and oxygen to give nitric oxide which combines with more of oxygen to produce nitrogen dioxide. Nitrogen dioxide dissolves in rain water to produce nitric acid. It is widely distributed in the form of its salts, viz., sodium nitrate, potassium nitrate and calcium nitrate.

6-8-1 LABORATORY PREPARATION OF NITRIC ACID

Nitric acid is prepared by gently heating equal masses of sodium (or potassium) nitrate and concentrated sulphuric acid in a glass retort. The vapours of nitric acid evolved are condensed as a light yellow liquid in a receiver cooled under tap water (Fig. 6-14).

$\text{NaNO}_3(s) + \text{H}_2\text{SO}_4(l) \rightarrow \text{NaHSO}_4(s) + \text{HNO}_3(l)$
Pure nitric acid is, however, a colourless liquid. The yellow colour is due to the dissolving of nitrogen dioxide, a reddish brown gas, in the acid. This gas is often produced due to the decomposition of nitric acid by the heat of reaction.

$4\text{HNO}_3(l) \rightarrow 4\text{NO}_2(g) + 2\text{H}_2\text{O}(g) + \text{O}_2(g)$
This is why gentle heating is advised.

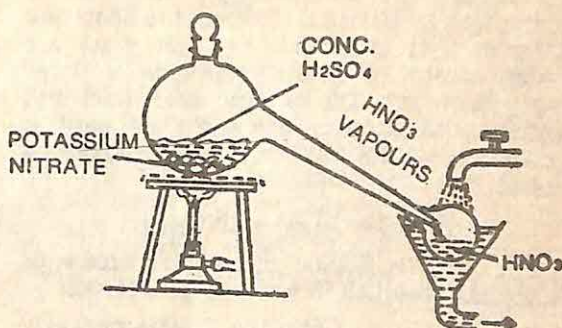
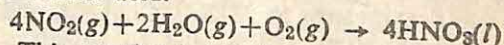


Fig. 6-14 Preparation of nitric acid

If air is bubbled through the yellow nitric acid obtained, the latter turns colourless because the nitrogen dioxide is oxidized to form nitric acid.



This reaction is just the reverse of decomposition of nitric acid.

6-8-2. MANUFACTURE OF NITRIC ACID

Nitric acid is made by the catalytic oxidation of ammonia (Ostwald's process). A mixture of purified air (10 parts by volume) and ammonia (1 part by volume) is passed through a chamber containing platinum gauze at 1000-1100K (Fig. 6-15). The ammonia is then oxidized to nitric oxide.

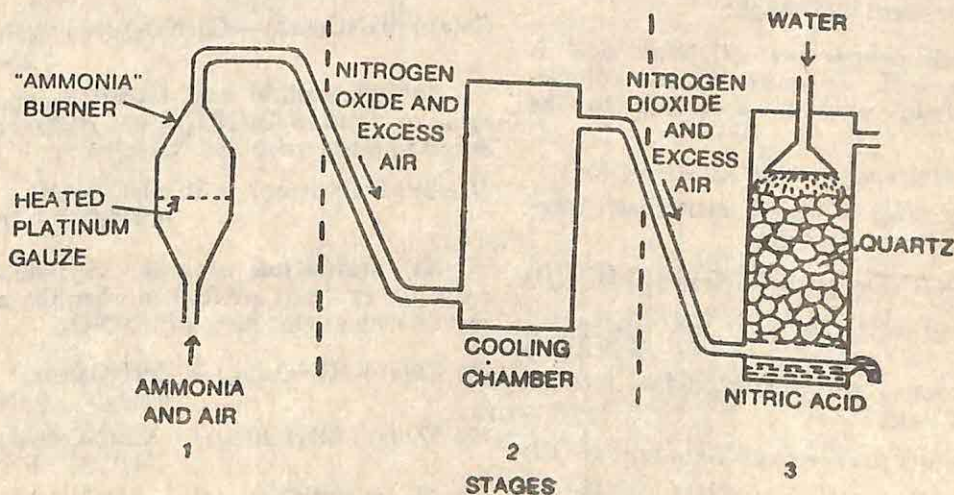
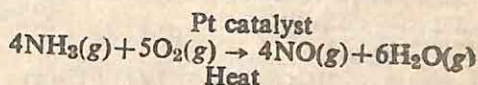
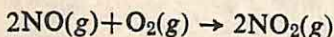
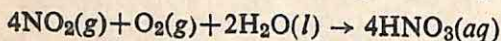


Fig. 6-15. Manufacture of nitric acid

The reaction is exothermic and the heat of the reaction maintains the required temperature of the catalyst chamber. The hot gases are rapidly cooled by passing through a large empty chamber. The nitrogen oxide does not combine with excess oxygen in the air until it is cooled to $\sim 323\text{K}$. Then nitrogen dioxide is formed.



The nitrogen dioxide, mixed with excess of air, is then absorbed in water to give HNO_3 .



6-8-3. PROPERTIES OF NITRIC ACID

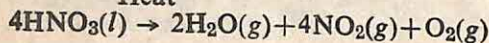
Pure nitric acid is a colourless, fuming and highly corrosive liquid. It attacks the skin leaving yellow stains. It boils at 359K . It freezes to a white solid at 231K . Concentrated nitric acid is often yellow due to dissolved nitrogen dioxide produced by its photochemical decomposition.

The so called commercial concentrated nitric acid contains about 70% by weight of pure acid and 30% water.

It is soluble in water in all proportions and the solution has a sour taste and turns blue litmus red.

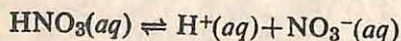
1. Stability. Pure nitric acid is unstable. It decomposes on heating.

Heat

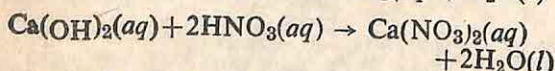
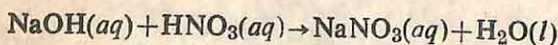


Hence, pure acid is not generally used. It is also decomposed by sunlight.

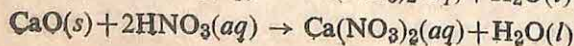
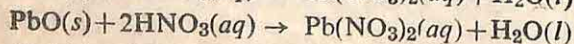
2. Acidic properties. (i) Nitric acid is a very strong acid. It ionizes almost completely in dilute solution according to the equation.



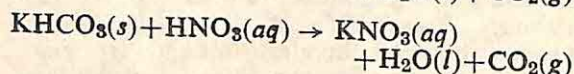
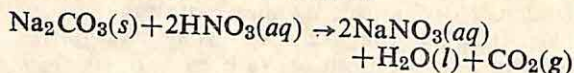
(ii) Like other acids, it neutralizes bases forming salts and water.



(iii) It reacts with basic oxides forming nitrates and water



(iv) It reacts with carbonates and bicarbonates liberating carbon dioxide.

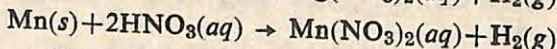
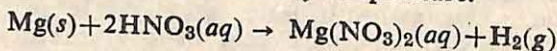


3. Oxidizing properties. Nitric acid behaves as an oxidizing agent whether it is concentrated or dilute. The following reactions illustrate its oxidizing nature :

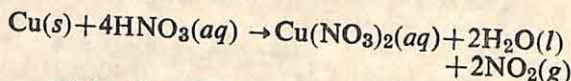
(a) Reaction with metals

Nitric acid reacts with all metals except gold and platinum. Its reaction with many metals is slowed down because it renders the surface passive. Aluminium if not attacked by the acid as its surface remains covered by a thin layer of aluminium oxide. Iron and chromium are made passive by the acid. The reaction products formed depend upon the concentration of the acid, the activity of the metal and the temperature.

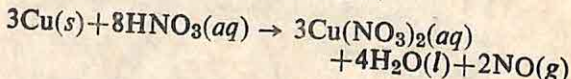
(i) **Oxidation of magnesium and manganese.** Very dilute nitric acid (say 5%) gives hydrogen on reacting with magnesium and manganese at ordinary temperature.



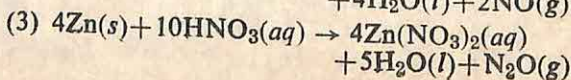
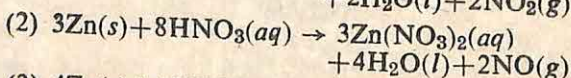
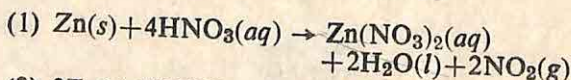
(ii) **Oxidation of copper.** With concentrated acid copper is oxidized to copper (II) nitrate and the nitric acid is reduced to nitrogen dioxide and water.

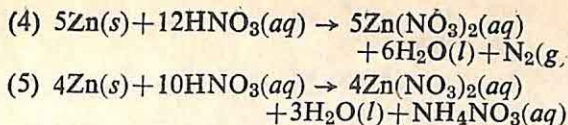


With dilute nitric acid ($\sim 50\%$) copper is again oxidized to $\text{Cu}(\text{NO}_3)_2$, but HNO_3 is reduced to nitric oxide and water.



(iii) **Oxidation of zinc.** A number of reduction products are formed when the active metals such as zinc react with HNO_3 .

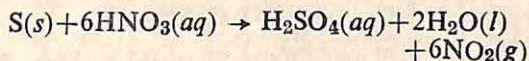




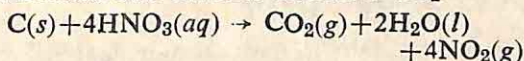
The concentration of the acid decreases from reaction (1) to (5)

(b) Reaction with non-metals

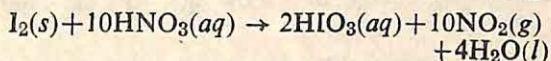
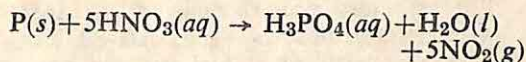
(i) Oxidation of sulphur. Powdered sulphur reacts with hot concentrated nitric acid to give dense brown fumes of nitrogen dioxide. Sulphur is oxidized to its oxyacid.



(ii) Oxidation of carbon. Hot concentrated nitric acid oxidizes carbon to CO_2 .

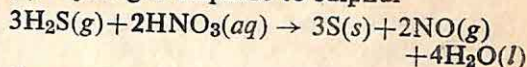


(iii) Oxidation of phosphorus and iodine. Both phosphorus and iodine are oxidized to phosphoric acid and iodic acid respectively.



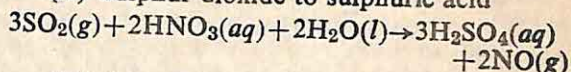
(c) Reaction with inorganic compounds. Concentrated nitric acid and even dilute nitric acid oxidizes many inorganic compounds and is itself reduced to nitric oxide.

(i) Hydrogen sulphide to sulphur



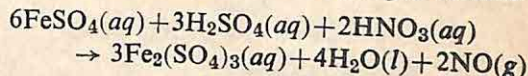
A saturated solution of hydrogen sulphide is prepared by bubbling H_2S gas through water. To this solution a few drops of concentrated HNO_3 is added. Hydrogen sulphide is oxidized to sulphur which precipitates and starts floating on the upper surface of the solution.

(ii) Sulphur dioxide to sulphuric acid



(iii) Iron (II) sulphate to iron (III) sulphate.

A small amount of nitric acid is added to a solution of iron (II) sulphate prepared in dilute sulphuric acid and the mixture is heated. The light green solution of iron (II) sulphate turns yellow or brown, due to oxidation of iron (II) sulphate to iron (III) sulphate. The nitric acid is reduced to nitric oxide which on reacting with air gives brown fumes of nitrogen dioxide.



6-8-4. TEST OF NITRIC ACID

1. Concentrated nitric acid on strong heating gives nitrogen dioxide and oxygen (Fig. 6-16). Nitrogen dioxide is recognized by its brown colour. Oxygen reignites a glowing splint.

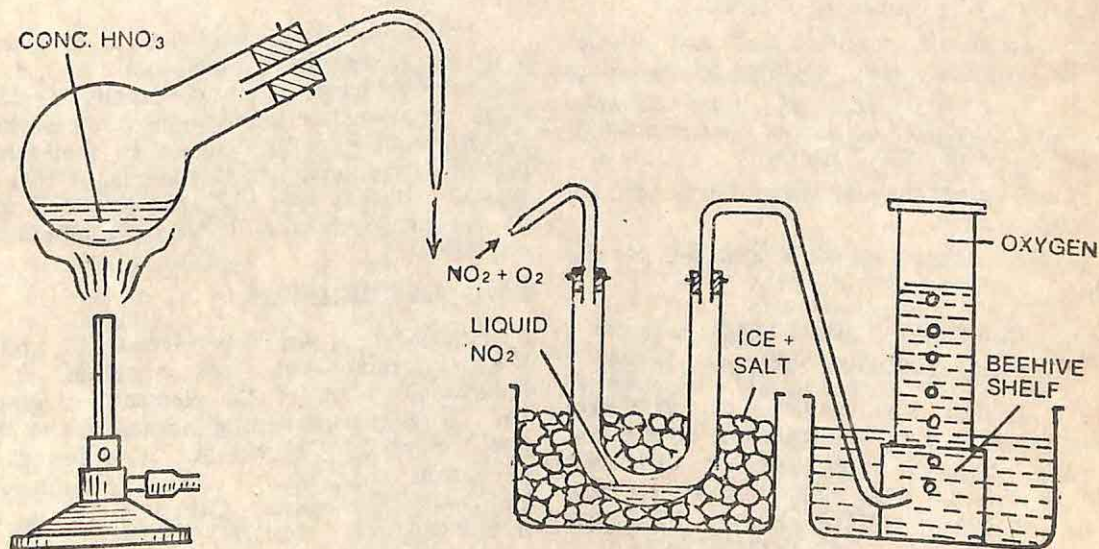
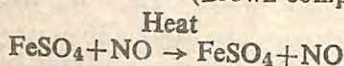
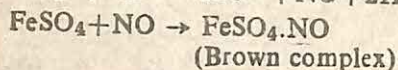


Fig. 6-16. Thermal decomposition of concentrated nitric acid

2. When some copper turnings are put in conc. nitric acid contained in a test tube and heated, dense brown fumes of nitrogen dioxide are evolved.

3. **Brown ring test.** To a cold solution of dilute nitric acid (NO_3^- ion) freshly prepared ferrous sulphate solution is added and then concentrated H_2SO_4 is added slowly along the walls of the tube. H_2SO_4 forms the lower layer (denser than aqueous solution of FeSO_4). On the junction of the two layers a *brown ring* appears. Some heat is produced which is sufficient to initiate the reduction of NO_3^- ion to NO (forms a brown complex with FeSO_4). On stirring the solution, the ring disappears as a result of heat produced during mixing of H_2SO_4 with aqueous solution and the whole solution becomes black. The following reactions take place :



6-8-5. EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers :

1. To demonstrate the oxidizing properties of nitric acid by using the following substances : (i) H_2S gas, (ii) copper turnings, and (iii) iron (II) sulphate solution (Section 6-8-3, Oxidizing properties of HNO_3).

2. To identify the nitric acid and nitrates by the brown ring test. (Section 6-8-4)

3. To study the effect of dilute and concentrated nitric acid on copper. (Section 6-8-3, Oxidizing properties of HNO_3).

4. To study the reaction of nitric acid on aluminium strip.

(Hint : Aluminium is not attacked by the acid).

6-8-6. USES OF NITRIC ACID

Nitric acid is chiefly used as given below :

1. In the manufacture of fertilizers (ammonium nitrate and calcium ammonium nitrate), explosives (nitroglycerin dynamite, TNT, picric acid, gun cotton), dyes, plastics, drugs, perfumes, textiles (cotton, wool and linen) synthetic fibres, photographic films.

2. In the extraction of certain metals.

3. In the refining of certain metals, e.g., Ag and Au.

4. In industries producing artificial silk and cellulose nitrate.

5. In the manufacture of chemicals, e.g., phosphoric acid from phosphorus and oxalic acid from carbohydrates.

6. In the manufacture of different nitrates which are used as fertilizers, and in some medicines, photography and in fireworks.

7. As a laboratory reagent.

8. For etching designs or names upon metals like copper, brass and bronze.

6-9. PHOSPHORUS

Symbol	P	Relative atomic mass	31
Molecular formula	P_4	Relative molecular mass	124
		Atomic number	15

Phosphorus was recognized in 1669 by Brand. Its name has been derived from its unique property of 'glowing' in the dark (phosphorescence).

Phosphorus, like nitrogen, is needed by all living beings because it enters the composition of some proteins (both vegetable and animal proteins).

Place in the periodic table and general characteristics

Phosphorus is the second element of group VA. Its electronic configuration is 2, 8, 5. The valence shell of its atoms contains 5 electrons. Phosphorus atoms unite into diatomic P_2 , tetratomic P_4 and polymeric P_n molecules. P_2 molecules have a structure similar to that of N_2 and exist only above 1273K. In the liquid or vapour form (below 1273K), P_4 molecules are stable.

6-9-1. OCCURRENCE

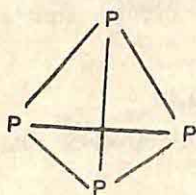
Phosphorus is the only element of group VA that does not occur free in nature. It is the most abundant of the elements in group VA. It ranks tenth among the elements in the earth's crust, 0.1% by weight. It is found in phosphate deposits, e.g., phosphorite $\text{Ca}_3(\text{PO}_4)_2$, fluorapatite, $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$, or hydroxyapatite $\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$.

Phosphorus is an essential constituent of bones, teeth, muscles, brain and nerve tissues.

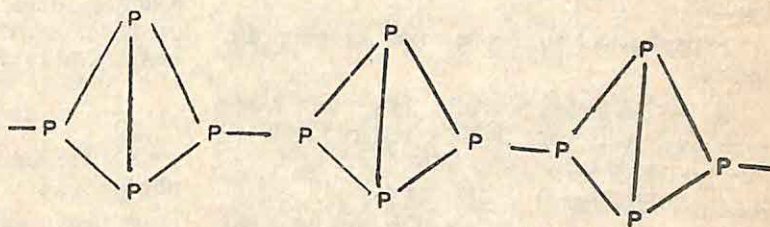
In animals, it is also present in proteins of milk and blood. In plants, phosphorus is contained chiefly in the seed proteins. The bones of animals (phosphorus as hydroxyapatite) and rock phosphates [$\text{Ca}_3(\text{PO}_4)_2$] are the main sources of phosphorus.

16-9-2 ALLOTROPY IN PHOSPHORUS

Phosphorus exists in several allotropic forms of which only two are important. These are white or yellow and red phosphorus. White phosphorus exists as P_4 molecules (tetrahedral). Red phosphorus has a polymeric type of structure resulting from the partial breakdown and interlinking of P_4 tetrahedra. The red variety is the stable form of phosphorus. White phosphorus is unstable and changes very slowly at room temperature to the stable form. Red phosphorus can be obtained by heating the white form, in the absence of air, for four or five days at 523K.



White or yellow phosphorus



Red phosphorus

Red phosphorus can be reverted back to white phosphorus by heating, in the absence of air, until it vapourizes and then condensing the vapour. A comparison of the properties of the two allotropes of phosphorus is given in Table 6-4.

6-9-3 CHEMICAL PROPERTIES OF PHOSPHORUS

1. **With Oxygen.** The most important property of white phosphorus is its reaction with oxygen. Because of its low ignition temperature, it catches fire in oxygen (or air) producing dense white fumes consisting of the oxides of phosphorus.

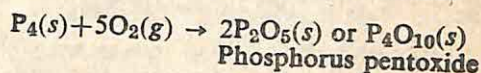
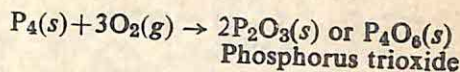
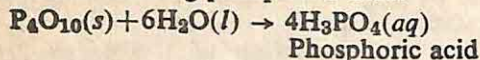


Table 6-4 Physical and chemical properties of white and red phosphorus

S. No.	Property	White phosphorus	Red phosphorus
1.	State and colour	White waxy solid	Purple-red amorphous powder
2.	Density (g/cm^3)	1.8	2.2
3.	Smell	Garlic-like	No smell
4.	Meeting point (K)	317	773–873 (under pressure)
5.	Toxicity	Very poisonous	Non-poisonous
6.	Solubility	Insoluble in water; soluble in CS_2 and other organic solvents	Insoluble in water and CS_2 and other organic solvents
7.	Ignition	Ignites at 308K; burns spontaneously in air	Ignites at 530K
8.	Phosphorescence	Greenish glow	No phosphorescence
9.	Reactivity	Very reactive	Less reactive.
10.	Storage	Under water	Can be stored easily
11.	Reaction with Cl_2	Ignites spontaneously giving PCl_3 and PCl_5	Reacts on heating forming PCl_3 and PCl_5
12.	Reaction with alkalis	Produces PH_3 on heating	No reaction

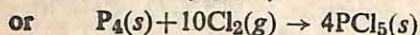
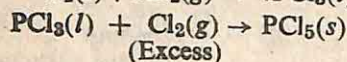
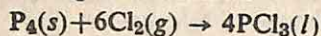
Phosphorus pentoxide reacts vigorously with water forming phosphoric acid.



White phosphorus glows in the dark because its vapours are oxidized by atmospheric oxygen with the emission of light.

Red phosphorus burns to give P_2O_5 , only when heated above 533K.

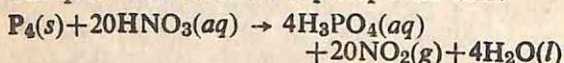
2. With chlorine. Phosphorus reacts with the halogens exothermally. White phosphorus ignites spontaneously in chlorine to form tri- and pentachlorides.



Red phosphorus also reacts with chlorine at high temperature forming tri- and pentachlorides.

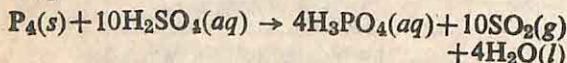
Phosphorus also reacts with bromine and iodine.

3. With acids. White phosphorus reacts explosively with conc. HNO_3 (reduced to NO_2). Phosphorus is oxidized to phosphoric acid.

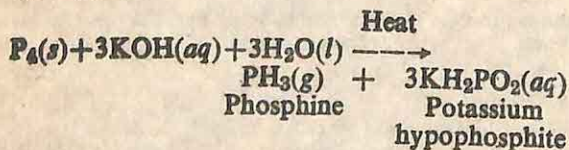


Concentrated HNO_3 reacts vigorously on warming with red phosphorus in the presence of a trace of iodine as catalyst.

Hot concentrated H_2SO_4 yields phosphoric acid with phosphorus and is itself reduced to SO_2



4. With alkalis. White phosphorus reacts with hot strong aqueous caustic soda (NaOH) or KOH to form phosphine (not hydrogen).



Red phosphorus does not react with alkalis.

6-3-4 USES OF PHOSPHORUS

Some of the important uses of phosphorus are listed below :

1. Phosphorus is used in the manufacture of phosphoric acid (used in the preparation of phosphatic fertilizers), phosphorus pentoxide (dehydrating agent), sodium metaphosphate (used for softening water), phosphor-bronze, a very hard alloy of copper, tin and phosphorus (being highly resistant to corrosion is used in making electrical gadgets), phosphine (used for producing smoke screen), etc.

2. It is used in making its chlorides and sulphides which are used in the manufacture of insecticides and plasticisers.

3. It is used in the manufacture of certain complex organic phosphates which are constituents of synthetic detergents.

5. Red phosphorus is used in the manufacture of tetra-phosphorus trisulphide, P_4S_3 which is used in making matches.

5. It is used in making rat poisons.

6. As the combustion of white phosphorus produces dense white smoke, phosphorus is used for making incendiary bombs, smoke bombs and fireworks.

WORK EXERCISES

1. List important sources of nitrogen and phosphorus.

2. Give reasons for the following :

- (i) Nitrogen is present in plenty in the atmosphere.
- (ii) Nitrogen is very stable and inert.
- (iii) Combustion reactions are slowed down by the presence of nitrogen.
- (iv) Traces of free nitric acid are found in the rain water after lightning.
- (v) Ammonia is not collected over water.
- (vi) Concentrated nitric acid lying in a reagent bottle becomes yellow.

(vii) Phosphorus does not occur free in nature.

3. Answer the following questions :

- (i) Is nitrogen lighter or heavier than air ?
- (ii) Is ammonia lighter or heavier than air ?
- (iii) Is ammonia acidic or basic ?
- (iv) Is magnesium nitride a starting material in the preparation of ammonia ?

- (v) Is nitrogen is used in the Haber's process ?
- (vi) Which compound of ammonia is used for making explosives ?
- (vii) Name the two metals which liberate hydrogen with dilute HNO_3 .
- (viii) Name the compound which gives dense white fumes with NH_3 .
- (ix) Give the reaction in which ammonia burns with a greenish flame.
- (x) Which of the two allotropic forms of phosphorus is more reactive ?
4. (i) In what form is the ammonia driven off from its aqueous solution ?
- (ii) Name the compound formed during the dry distillation of coal.
- (iii) Name the compound produced during lightning.
- (iv) What is nitrolime ? Give its use.
- (v) Give a few reactions which support the reducing nature of ammonia.
- (vi) Give a few reactions of nitric acid and non-metals which support the oxidizing nature of HNO_3 .
- (vii) What happens when white phosphorus reacts with caustic soda ?
5. How will you get O_2 , N_2 and H_2 using HNO_3 ?
6. Suggest a method using HNO_3 for the preparation of the following :
- (i) CO_2 , (ii) NO_2
(iii) S (iv) NH_4NO_3 .
7. Suggest a method using ammonia for the preparation of the following :
- (i) N_2 (ii) NH_4NO_3
(iii) HCl (iv) HNO_3
8. Justify the placement of nitrogen and phosphorus in the same periodic group.
9. (a) Which allotropic forms of phosphorus is used in safety matches ?
- (b) What are the names of the elements whose atomic number are 7 and 15 respectively. Give the significance of their names ?
- (c) What happens when :
- (i) P_4O_{10} reacts with water.
(ii) H_2S reacts with HNO_3 .
(iii) Concentrated nitric acid is heated.
(iv) Sodium nitrate is treated with dilute H_2SO_4 .
(v) CuSO_4 solution is treated with an excess of ammonium hydroxide.
(vi) Phosphorus is treated with H_2SO_4 .
10. (i) Describe briefly the preparation of ammonia in the laboratory.
(ii) Suggest a method for preparing an aqueous solution of ammonia in the laboratory.

OXYGEN AND SULPHUR

(Group VIA Non-metals)

6-10. OXYGEN

Symbol O	Relative atomic mass	15.999
Molecular O_2	Relative molecular mass	31.998
formula	Atomic number	8

Scheele discovered oxygen some time during the period 1771-3 but did not disclose about his discovery until 1777. In the meantime, Joseph Priestley prepared oxygen on 1st August, 1774 by heating mercuric oxide with sun-rays. He also produced oxygen by heating red lead. He named the gas 'dephlogisticated air'. Priestly related his discovery to Lavoisier, who considered its significance in relation to his own work—combustion, respiration and calcination of metals. Lavoisier recognized the gas as an element, finally naming it oxygen (Greek, oxys means sour or acid, genon means to form) as the products of combustion appeared to him to be acidic.

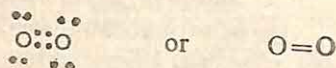
Oxygen is the most indispensable of all the elements for almost all forms of life. Living organisms derive energy for their vital functions through oxidation of substances by oxygen (through respiration) in their body.

Place in the periodic table and general characteristics

Oxygen is a typical non-metal. Its electronic arrangement is 2, 6 with 6 electrons in the valence shell. It is placed in group VIA of the periodic table.

Oxygen shows allotropy. It is a diatomic molecule. It exists in the form of discrete

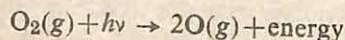
molecules. Two oxygen atoms are joined together by double bonds.



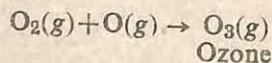
6-10-1. OCCURRENCE

Oxygen occurs in the native state in the atmosphere as diatomic molecules, $\text{O}_2(\text{g})$ forming about one fifth of the atmosphere by weight. It also exists in the combined form in water and in the soil and rocks of crust of the earth (50% by weight). In earth's crust, it mainly exists as oxides and oxyanions. Quartz and sand (SiO_2) are the important oxides. Examples of compounds in which oxygen is present in the oxyanions are nitrate, NO_3^- ; carbonate, CO_3^{2-} ; sulphate, SO_4^{2-} ; orthophosphate, PO_4^{3-} ; and silicates SiO_3^{2-} .

Atmospheric oxygen contains the three isotopes of oxygen: ^{16}O , ^{17}O and ^{18}O . In the upper atmosphere, a small amount of atomic oxygen is formed due to the action of ultra-violet light from the sun and cosmic rays causing dissociation.

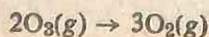


These atoms are captured by other O_2 molecules forming ozone, an allotrope of oxygen.



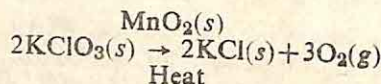
6-10-2. ALLOTROPY IN OXYGEN

Oxygen has two allotropes, i.e., oxygen (O_2) and ozone (O_3). Oxygen is the usual and most abundant form of oxygen. It has a special significance for life on earth. Ozone is mainly present in the upper part of the atmosphere. It is formed by the action of ultraviolet rays on oxygen (i.e., oxygen can be converted into ozone). It may also be prepared by passage of an electric discharge through oxygen at low pressure. It exists as triatomic molecules. It helps in preserving life on the earth by absorbing much of the harmful ultraviolet rays in sunlight. Ozone is a highly reactive substance. It acts as a powerful oxidizing agent. It decomposes giving oxygen on heating.



6-10-3. PREPARATION OF OXYGEN

Oxygen is prepared in the laboratory by heating a mixture of potassium chlorate and manganese dioxide in the ratio of 4 : 1.



Manganese dioxide acts as a catalyst. In the presence of manganese dioxide catalyst, KClO_3 decomposes at a comparatively low temperature. It is collected in gas jars by the downward displacement of water (Fig. 6-17).

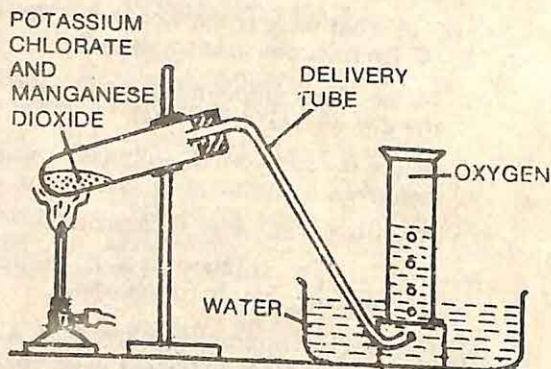


Fig. 6-17. Preparation of oxygen.

Oxygen is obtained commercially by liquefaction of air and subsequent fractional distillation of the liquid to separate O_2 from N_2 . Very pure oxygen is produced by electrolysis of water.

6-10-4. PROPERTIES OF OXYGEN

Oxygen is a colourless and odourless gas and is slightly heavier than air. It is slightly soluble in water (~4%). It is neutral toward litmus. It liquefies at 90K to a pale blue liquid and freezes at 54K to a blue solid.

It does not burn but supports combustion. Oxygen is a very active element and combines with many other elements both metallic and non-metallic and a large number of compounds.

1. Combustion of non-metals in oxygen. All non-metals except the halogens, noble-gases and nitrogen burn in oxygen. A small piece of phosphorus is ignited in a deflagrating spoon and is then inserted into a gas jar full of oxygen. It burns with a brilliant flame (Fig. 6-18) producing a dense white smoke of oxides.

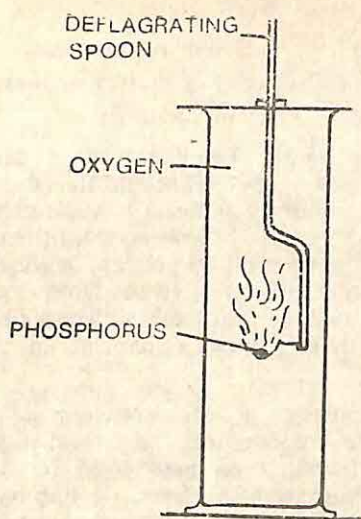
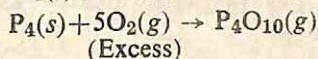
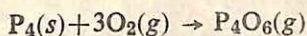
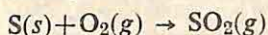


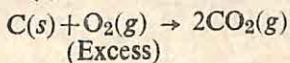
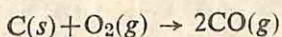
Fig. 6-18. Burning of phosphorus in oxygen



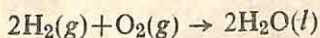
A small piece of sulphur burning with a pale blue flame is plunged into a gas jar full of oxygen. It burns much more brightly to give a gas with choking smell.



A small lump of carbon heated to red heat glows more brightly in the presence of oxygen, forming carbon monoxide or carbon dioxide.

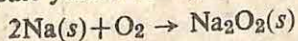


Oxygen reacts readily with hydrogen forming water.



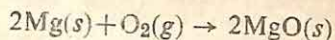
2. Combustion of metals in oxygen.

Active metals and some other metals burn in oxygen. Noble metals such as gold, platinum, etc. are immune to oxygen. A small piece of sodium is heated in a deflagrating spoon. It first melts to a silvery liquid and then burns with a yellow flame. When placed in oxygen it burns much more brightly giving sodium peroxide (pale yellow solid),



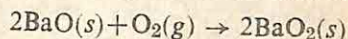
A small piece of magnesium is ignited and made to react with oxygen. It burns even more

brilliantly forming a white powder, magnesium oxide.

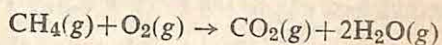


Oxygen combines slowly with copper and mercury on heating. It reacts spontaneously with lead (molten form), on heating, forming lead monoxide.

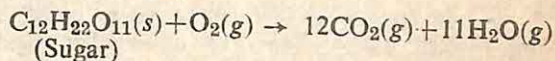
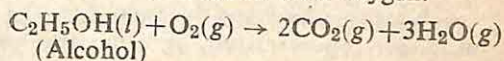
3. Combustion of compounds in oxygen. Many compounds when they are burnt or roasted in oxygen form the oxides of their constituent elements. Sometimes oxygen combines with the compounds as a whole, e.g.



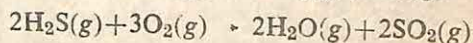
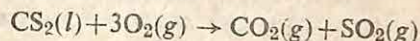
Hydrocarbons burn in oxygen giving a mixture of carbon dioxide and steam.



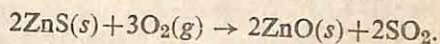
Some other organic compounds form carbon dioxide and steam with oxygen.



Carbon disulphide and hydrogen sulphide, when burnt in a plentiful supply of oxygen, yield sulphur dioxide.

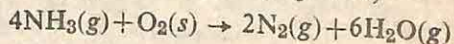


Metallic sulphides when roasted in air give sulphur dioxide and the metal oxide.

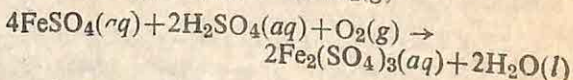
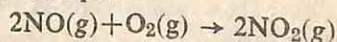


(This type of reaction is useful in the extraction of metals).

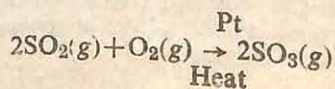
Oxygen oxidizes some other compounds also, e.g., ammonia, when burnt in oxygen, yields nitrogen and steam (Fig. 6-11)

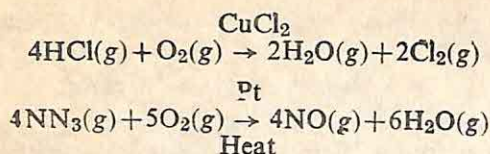


More examples :



Oxygen oxidizes some compounds in the presence of a catalyst, e.g.,





6-10-5. USES OF OXYGEN

Most of the uses of commercial oxygen are based upon the property that the element acts as an oxidizing agent. Some of the important uses are listed below :

1. In the manufacture of nitric acid, methyl alcohol, ethylene oxide and other chemicals.
2. As a propelling fuel in rockets, satellites, missiles, etc. in the form of liquid oxygen.
3. In oxy-acetylene torches for the high temperature welding and cutting of metals.
4. In bleaching and in thickening of oils used in making varnishes, linoleum, etc.
5. In making explosive cartridges by mixing it with carbon dust to be used in coal mining in place of dynamite.
6. Vital for combustion processes.
7. Used in the production of steel because it removes carbon and other impurities more rapidly than air.
8. Used in the extraction of metals.
9. Used as an oxidizing agent for many processes.
10. Makes drinking water more palatable. Helps in destroying harmful bacteria and decaying animal and vegetable matter in soil, rivers and harbours by oxidation.
11. Used as an aid to respiration where the amount of oxygen in air is insufficient, e.g., at high altitudes, in deep mines, in submarines, etc. Mountaineers, astronauts, deep-sea divers and miners, etc. take self-contained oxygen equipment for breathing.
12. Used as an aid to respiration in medical and dental practice. It is supplied where lungs are weak or injury makes artificial respiration impracticable and in the resuscitation of victims of coal gas poisoning and other accidents. Dinitrogen oxide and other anaesthetics are administered with oxygen.

6-11. SULPHUR

Symbol S	Relative atomic mass	32.1
Molecular S ₈	Relative molecular mass	256.8
formula	Atomic number	16

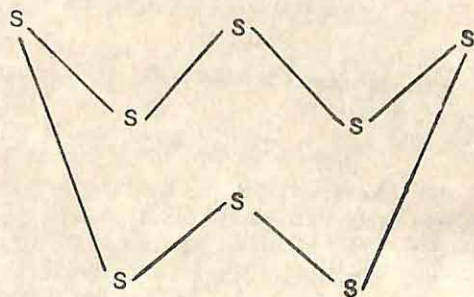
Sulphur has been known since early times, being used by Egyptians and the Greeks as a yellow colouring material. Alchemists tried to incorporate its 'yellowness' into other substances in attempts to produce gold. The name 'sulphur' has been derived from the sanskrit word, 'sulvari, which means 'enemy of copper'. Lavoisier recognized sulphur as an element in 1777.

Because of its occurrence near volcanoes, sulphur commanded the awe of ancient man. Sulphur has been proved to be one of the cornerstones of chemical technology, mainly because of the industrial importance of sulphuric acid and the agricultural importance of sulphate fertilizers.

Place in the periodic table and general characteristics

Sulphur is the element of group VIA. Its electronic configuration is 2, 8, 6. The outermost shell of its atom contains 6 electrons. It tends to add two electrons to form S²⁻ ions or form two covalent bonds to attain their octets of electrons.

The atoms of sulphur usually do not show multiple bonding like oxygen. Sulphur in the solid state exists as S₈ which has the following structure known as the puckered ring structure.



The S₈ rings also persist in the liquid and gaseous states.

6-11-1 OCCURRENCE

Sulphur is found extensively in the earth's crust both in the free elemental state and in the combined state. Free sulphur occurs in

large natural deposits near volcanoes and can be mined without further purification. The large sulphur deposits occur near the Gulf of Mexico and in Sicily. Its deposits are also found in Japan, Italy and USA (Texas and Louisiana). In the combined state, sulphur occurs as sulphides (iron pyrites, FeS_2 ; galena, PbS ; zinc blende, ZnS ; copper pyrites, CuFeS_2 ; etc.) and sulphates (barite, BaSO_4 ; gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) of metals. To some extent it also occurs in volcanic gases as hydrogen sulphide, H_2S and sulphur dioxide, SO_2 .

Sulphur is also a constituent of much naturally occurring organic matter such as petroleum (in the form of H_2S) and coal. Its presence in fossil fuels causes environmental and health problem because sulphur and its compounds undergo combustion giving sulphur dioxide, an air pollutant.

It is also present in various forms in plants and animals. It is present in onion, garlic, mustard, egg, protein, oils, etc.

6-11-2 EXTRACTION OF SULPHUR

Since the deposits of sulphur are usually found at a depth of 150-500 metres below the surface of the earth, under layers of quicksand and gravel, this makes its direct mining impossible. It is extracted by the Frasch process. Three concentric pipes are sunk to reach the deposits. Superheated water under pressure is forced down the outer pipe and compressed air is blown down the central shaft (innermost pipe). Water melts the sulphur. The molten sulphur forms a froth with the compressed air. The compressed air also forces up this froth to the surface through the middle-pipe. It is then allowed to cool and solidify into vats. This sulphur is of about 99.9% purity. This method is used in USA.

Small amount, but a highly pure sample of sulphur can be obtained by burning hydrogen sulphide in a limited supply of air.

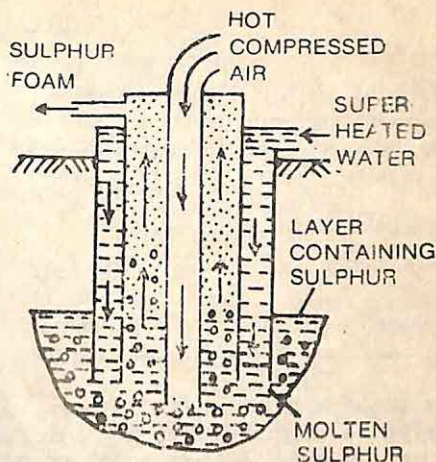
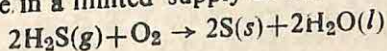
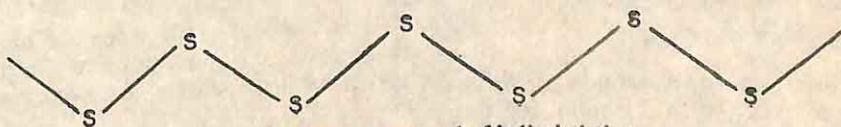


Fig. 6-19 Extraction of sulphur by Frasch process

6-11-3 ALLOTROPY IN SULPHUR

Sulphur can exist in several allotropic forms. There are perhaps over a dozen different sulphur allotropes. The most common of the well-characterized sulphur allotropes are the *orthorhombic* and *monoclinic* forms. Both contain covalently bound S_8 puckered rings, the difference in the allotropes being a difference in the crystal packing of the S_8 units. Orthorhombic sulphur, the most stable form at ordinary temperature, changes to the monoclinic above 368.6K. However, the inter-conversion between the two forms is slow. These two forms are soluble in non-polar solvents such as benzene, carbon disulphide, ether and alcohol.

A third unstable but important allotrope is called *plastic sulphur*. This is an amorphous solid obtained from a supercooled liquid. This is a sticky elastic substance which can be drawn into long threads. It contains long helical chains of sulphur atoms.



Plastic sulphur—composed of helical chains

Table 6-5 Physical properties of allotropes of sulphur

Property	Rhombic	Monoclinic	Plastic
Colour	Pale yellow	Yellow	Yellowish-brown
State	Octahedral crystals	Needle-like crystals	Rubber-like mass
Melting point, K	387.5	392	No definite m.p.
Density (g/cm ³)	2.06	1.98	1.95
Solubility in carbon disulphide	Soluble	Soluble	Insoluble

It is insoluble in non-polar solvents. After a few days the long chains slowly disintegrate and reform the small S₈ rings which crystallize gradually in rhombic lattice. A comparison of the physical properties of the allotropes of sulphur is given in Table 6-5.

6-11-4 PROPERTIES OF SULPHUR

Sulphur is a pale yellow solid with no odour. It is insoluble in water. It is soluble in carbon disulphide, acetone, and carbon tetrachloride. When crushed roll sulphur (commercial form) is heated in the absence of air the following changes takes place :

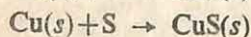
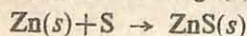
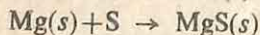
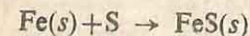
(i) At 387K, it melts to an amber-yellow mobile liquid.

(ii) At 453K, it becomes a thick black liquid which does not flow out of the test tube.

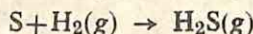
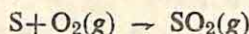
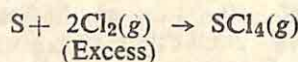
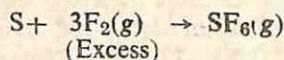
(iii) Near the boiling point, 717K, the black mass again becomes mobile and reddish-brown in colour. On further heating, it starts boiling and yellow vapours of sulphur are given off.

Sulphur burns in air with a blue flame from sulphur dioxide.

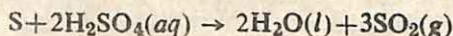
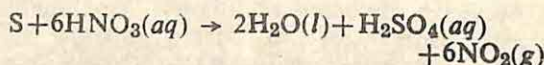
1. Reaction with metals. Sulphur combines with many metals giving sulphides on heating.



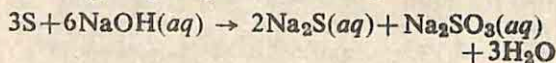
2. Reaction with non-metals. Various non-metals that react with burning (or pre-heated) sulphur include fluorine, chlorine, bromine, hydrogen, oxygen, carbon, phosphorus, etc. It reacts less readily with non-metals than oxygen.



3. Reaction with acids. Sulphur does not react with aqueous hydrochloric acid but reacts with oxidizing acids.



4. Reaction with alkalis. Sulphur reacts with hot concentrated solutions of alkalis giving sulphides and sulphites.



6-11-5 USES OF SULPHUR

(i) Sulphur is widely used in the manufacture of sulphur dioxide and sulphuric acid.

(ii) Sulphur is used to produce very hard vulcanite or ebonite (vulcanising rubber).

(iii) Sulphur is used in producing important chemicals. These include carbon disulphide, sulphur dyes, calcium and magnesium bisulphites (bleaching agents), phosphorus trisulphide (used in match industry), etc.

(iv) Sulphur is used in the manufacture of explosives, e.g., gunpowder (sulphur, carbon and potassium nitrate), fireworks and matches.

(v) It is used as a germicide and insecticide for controlling growth of fungus in plants.

(vi) It is widely used in medicines—in ointments for treating skin diseases and for

manufacturing sulphur drugs. Sulphur and its compounds are commonly used in the Ayurvedic system. Mercuric sulphide is used as an Ayurvedic medicine under the name of Makaradhwaj.

6-11-6 COMPOUNDS OF SULPHUR

Sulphur forms a large number of compounds. Hydrogen sulphide, sulphur dioxide and sulphuric acid are amongst the important compounds. Their chemistry is being discussed in the following pages.

6-12 HYDROGEN SULPHIDE

Molecular formula H_2S .

Relative molecular mass 34.1

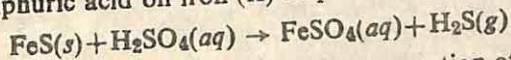
Electron dot structure



Hydrogen sulphide is an important compound of sulphur with hydrogen. This compound occurs naturally in some volcanic gases and in certain mineral waters. Petroleum gases also contain hydrogen sulphide. Air also contains hydrogen sulphide in small quantities. This hydrogen sulphide is formed by the decay of plants and animals containing sulphur proteins.

6-12-1 LABORATORY PREPARATION OF HYDROGEN SULPHIDE

Hydrogen sulphide is usually prepared by the action of dilute hydrochloric or dilute sulphuric acid on iron (II) sulphide.



The apparatus used for the preparation of the gas is portrayed in Fig. 6-20. It consists of

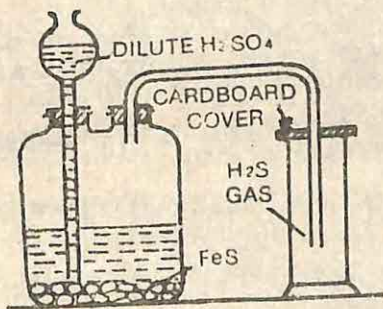


Fig. 6-20 Preparation of hydrogen sulphide gas in the laboratory

a Woulfe's bottle fitted with a thistle funnel and a delivery tube. A flat bottomed flask can also be used in place of Woulfe's bottle. Iron sulphide is placed in Woulfe's bottle and dilute H_2SO_4 or HCl is poured through the thistle funnel. The thistle funnel is always kept dipped into the solution to avoid the evolution of gas formed through the stem of the funnel.

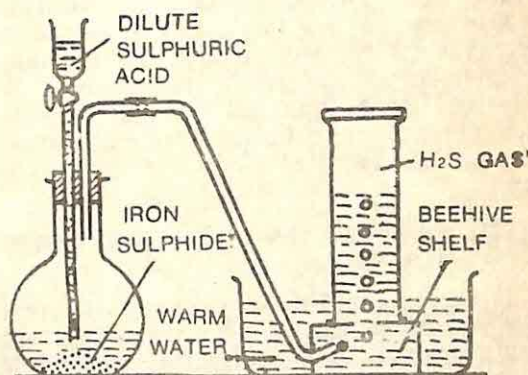


Fig. 6-21 Preparation of hydrogen sulphide in the laboratory

The gas is collected by upward displacement of air. Alternatively, it may be collected over hot water (Fig. 6-21), hydrogen sulphide being fairly soluble in cold water. The gas may be dried over phosphorus pentoxide.

Intermittent supply of hydrogen sulphide

Hydrogen sulphide is often required in the laboratory. For this reason, the gas is usually prepared in a Kipp's apparatus. Pieces of iron

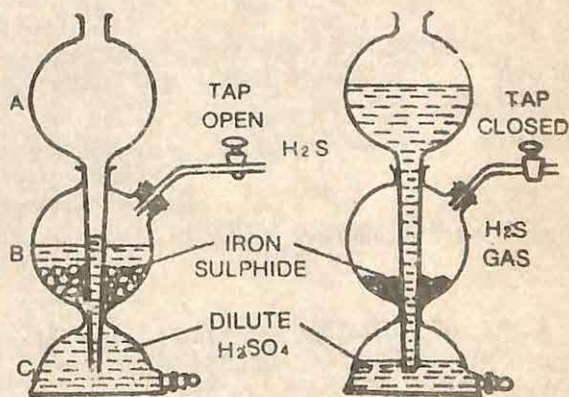


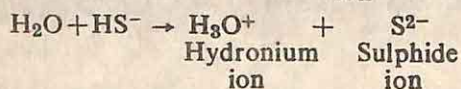
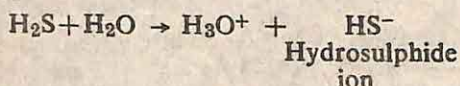
Fig. 6-22 Continuous supply of H_2S gas in the laboratory

sulphide are placed in the central compartment (B) and dilute sulphuric acid is poured through the upper compartment (A). The upper part A of the assembly can be detached. Its stem goes upto the bottom of compartment C and through this stem acid reaches compartment B via compartment C. When the tap T is opened, the acid rises into the compartment B. Here the acid reacts with iron sulphide to produce H_2S . The gas is taken out through the side tube. When the apparatus is not in use, the tap T is closed. On closing the tap, the pressure of the gas in compartment B increases. As a result of this, the acid goes back into the compartment A through compartment C, and the production of the gas stops.

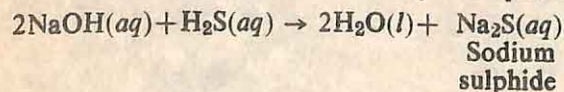
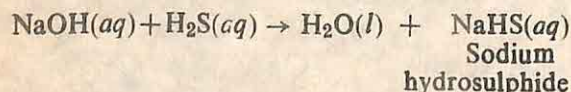
6-12-2 PROPERTIES OF HYDROGEN SULPHIDE

Hydrogen sulphide is a gas and therefore, a covalent compound. It has a characteristic repulsive odour like that of rotten eggs. It is colourless and poisonous in nature. If inhaled in excess, it may be fatal. It is heavier than air and soluble in cold water.

1. **Acidic nature.** It is fairly soluble in water and its solution is weakly acidic in nature. The acidity is caused by the slight ionization of the dissolved gas to give hydrogen ions (or hydronium ions). It turns blue litmus paper red.

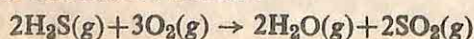


2. **Reaction with alkalis.** An aqueous solution of H_2S (acidic) reacts with alkalis forming salt and water.

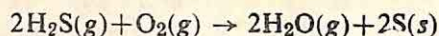


3. **Combustibility.** It is not a supporter of combustion but itself burns in air with a pale blue flame.

In a plentiful supply of air, steam and sulphur dioxide are formed.



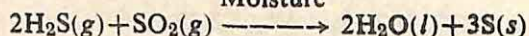
In a limited supply of air, free sulphur is deposited.



4. **Reducing nature.** In many of its reactions, H_2S gives up its hydrogen to reacting substances, and gets itself oxidized to sulphur. For example .

(i) If a gas jar of H_2S is mixed with one of SO_2 in the presence of moisture, a yellow deposit of sulphur is obtained.

Moisture

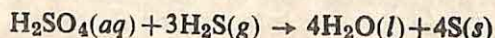


Sulphur dioxide is a powerful reducing agent, but differs from H_2S in that sulphur is deposited only in the presence of moisture.

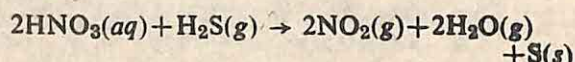
(ii) Halogens also react with H_2S giving free sulphur.



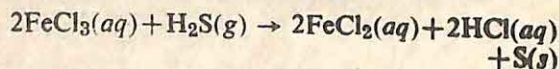
(iii) Concentrated sulphuric acid is reduced to sulphur when H_2S gas is bubbled through acid.



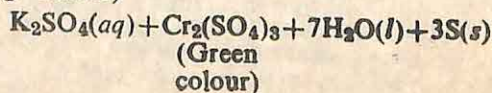
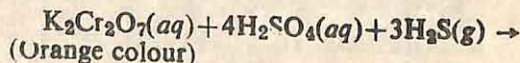
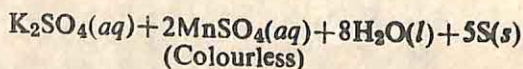
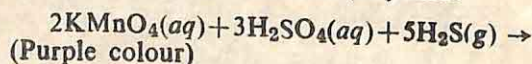
Nitric acid is also reduced to nitrogen dioxide.



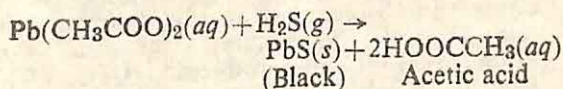
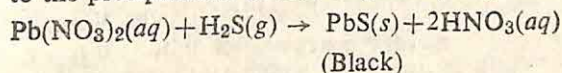
(iv) When H_2S is bubbled through a solution of ferric chloride (yellow coloured solution), a pale green solution of ferrous chloride is obtained. A pale yellow deposit of sulphur settles at the bottom.



(v) It also reduces acidified solutions of permanganates (VII) and dichromates (VI) to manganese (II) and chromic (III) salts.

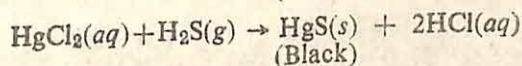
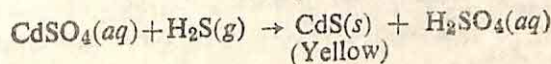
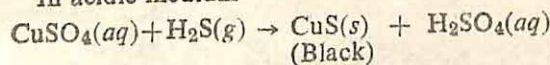


5. Reaction with metal salt solutions.
It reacts with many salt solutions forming insoluble coloured sulphides. Some sulphides are precipitated in acidic medium and some others are precipitated in alkaline medium. When H_2S is bubbled through a solution of lead acetate or lead nitrate it turns black due to the precipitation of lead sulphide (PbS).

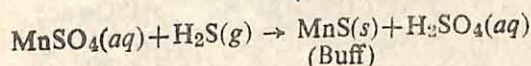
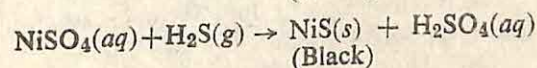
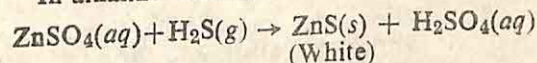


In a similar fashion, H_2S reacts with other metal salt solutions.

In acidic medium



In alkaline medium



Such reactions of hydrogen sulphide are used in qualitative inorganic analysis for identifying the various metallic ions.

6-12-3 TEST FOR HYDROGEN SULPHIDE

H_2S can be detected by its characteristic smell like that of rotten eggs.

When a strip of filter paper soaked into a solution of lead acetate is exposed to the vapours of H_2S contained in a gas jar, it turns black due to the formation of lead sulphide.

6-12-4 EXPERIMENTS

The followings experiments can be performed by the students in the laboratory after receiving instructions from their class teachers.

1. To prepare a sample of hydrogen sulphide gas (Section 6-12-1).

2. To show the presence of H_2S gas (Section 6-12-3).

3. To show the acidic behaviour of hydrogen sulphide.

[Hint : A saturated solution of hydrogen sulphide is prepared by bubbling H_2S gas through water contained in a test tube. A blue litmus paper turns red in this solution showing that the solution is acidic].

4. To study the reducing nature of hydrogen sulphide gas using sulphur dioxide gas and bromine water and other substances (Section 6-12-2, Reducing nature).

[Hint : A gas jar full of H_2S is inverted over a gas jar containing a few drops of bromine liquid. Bromine vapours mix with H_2S gas. After some time free sulphur is deposited along the walls of the gas jar].

5. To study the precipitation of some metal sulphides (Section 6-12-2, Reaction with metal salt solutions).

6. To observe some other physical and chemical properties (Section 6-12-2).

6-12-5 USES OF HYDROGEN SULPHIDE

Hydrogen sulphide is used as listed below :

1. Used as a laboratory reagent in the identification of certain metal ions, e.g., Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Co^{2+} , etc. (Qualitative inorganic analysis).

2. Used as a reducing agent.

3. Used for the preparation of metallic sulphides, many of which find use as paint pigments.

6-13 SULPHUR DIOXIDE

Molecular formula	SO_2
Relative molecular mass	64.00
Electron dot structure	

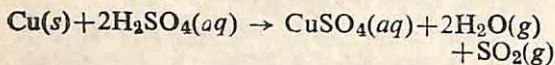


Sulphur dioxide is an important gas which is used mainly for the manufacture of sulphuric acid. It occurs in volcanic gases. Many hot springs contain dissolved sulphur dioxide. Atmospheric air also contains traces of this

gas which is produced by the burning of coal and other fuels during the roasting of metallic sulphides. Atmosphere over industrial towns is rich in sulphur dioxide. This gas is one of the major air pollutants.

6-13-1 LABORATORY PREPARATION OF SULPHUR DIOXIDE

Sulphur dioxide is usually prepared in the laboratory by heating concentrated sulphuric acid with copper turnings (copper is used in the form of turnings to make a large surface area available for the reaction).



The assembly used for preparing the gas is shown in Fig. 6-23. Copper turnings are placed in a round bottom flask which is then fitted with a delivery tube and a thistle funnel. Dilute sulphuric acid is poured through the thistle funnel which is almost touching the bottom of the flask. A hard boiling tube can also be used in place of a round bottom flask. The contents are heated first gently followed by strong heating. Sulphur dioxide is evolved with a strong effervescence. The gas is collected in a gas jar by upward displacement of air as it is heavier than air. It is not collected over water as it is highly soluble in water. The gas may be purified and dried by passing it through concentrated H_2SO_4 .

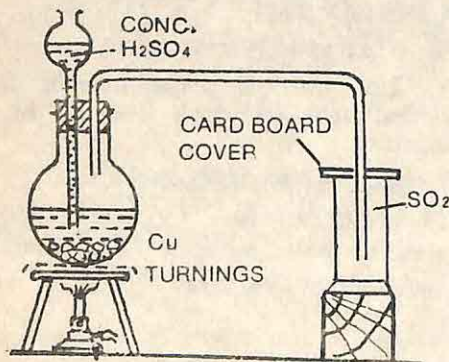
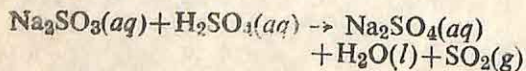


Fig. 6-23. Preparation of sulphur dioxide in the laboratory

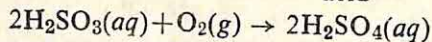
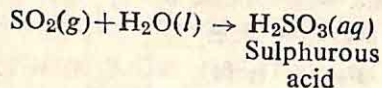
The gas can also be conveniently made in the laboratory by treating sodium sulphite with dilute H_2SO_4 .



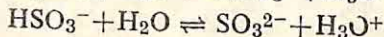
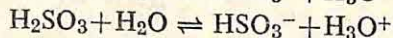
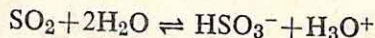
6-13-2 PROPERTIES OF SULPHUR DIOXIDE

Sulphur dioxide is a colourless gas with a sharp choking smell of burnt sulphur. It is poisonous and causes inflammation of the lungs and other disorders. It is heavier than air and highly soluble in water. It can be readily liquefied. Liquid SO_2 boils at 264K.

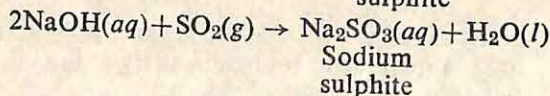
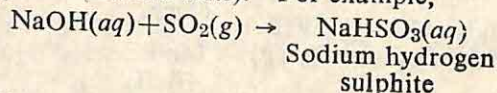
1. **Acidic nature.** Sulphur dioxide is highly soluble in water (fountain experiment discussed in Section 6-7-3). Its aqueous solution is acidic in nature. The solution so obtained is of sulphurous acid, H_2SO_3 . This acid is unstable. It only acts in situ. It is slowly converted into sulphuric acid on exposure to air.



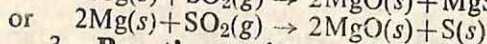
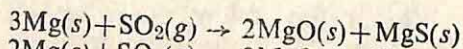
Sulphurous acid ionizes to form hydronium ion.



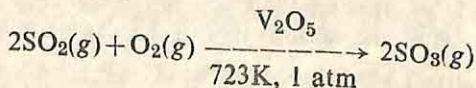
Its solution turns moist blue litmus paper red. It neutralizes alkalis to form two series of salts—hydrogen sulphites (acid salts) and sulphites (normal salts). For example,



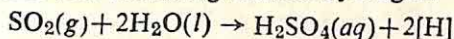
2. **Combustibility.** Sulphur dioxide is neither combustible nor a supporter of combustion. However, a piece of magnesium ribbon continues to burn in sulphur dioxide, which is decomposed by the heat of burning metal.



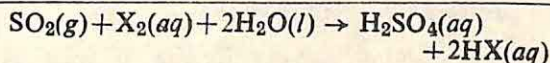
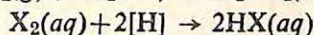
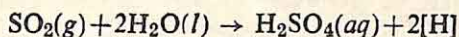
3. **Reaction with oxygen.** Sulphur dioxide combines with oxygen in the presence of a platinized asbestos or vanadium pentoxide at a temperature of about 723K and at a atmospheric pressure.



4. **Reducing nature.** Sulphur dioxide acts as a reducing agent in the presence of moisture because it is easily oxidized to sulphuric acid liberating nascent hydrogen.



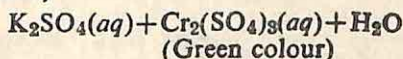
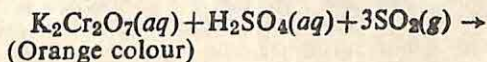
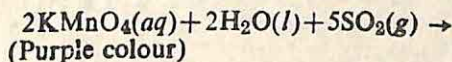
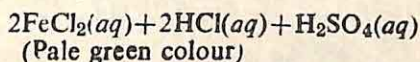
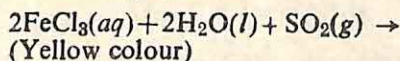
(i) It reduces halogens to halogen acids. When sulphur dioxide is bubbled through a pale green solution of chlorine water, the gas is absorbed. The chlorine water turns colourless forming a mixture of hydrochloric acid and sulphuric acid.



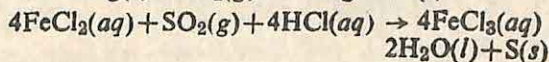
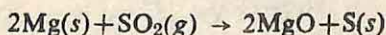
where $\text{X} = \text{Cl}, \text{Br} \text{ or } \text{I}$.

An aqueous solution of SO_2 decolourizes the coloured solutions of bromine and iodine forming colourless corresponding halogen acids (hydrides).

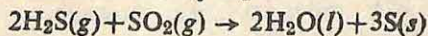
(ii) It also reduces ferric (III) salts and acidified solutions of permanganates (VII) and dichromates (VI) to ferrous (II), manganese (II) and chromic (III) salts.



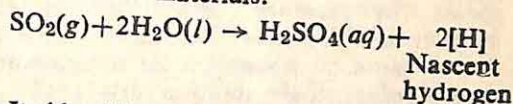
5. **Oxidizing nature.** SO_2 can act as an oxidizing agent. For example, metals such as iron (red hot), magnesium (ignited), etc. continue to burn in SO_2 to give mixed sulphides and oxides (or sulphur and oxide). In very strong acidic solution SO_2 can oxidize ferrous, cuprous and other ions.



SO_2 is reduced to S by H_2S .



6. **Bleaching action.** The bleaching action is due to the reduction of the colours of substances by nascent hydrogen which is formed when SO_2 reacts with water. Hence, it only bleaches moist materials.



Its bleaching action is temporary and mild. Hence, it is used for delicate things such as flowers, wool, etc. It can also bleach sugar, straw, paper, etc. The bleaching action also confirms the reducing nature of sulphur dioxide.

The bleached product slowly regains its colour on exposing to air due to oxidation. Bleached product + Atmospheric oxygen

Oxidation

—————> Original product

6-13-3 TEST FOR SULPHUR DIOXIDE

1. It has a characteristic pungent odour of burning sulphur.

2. It has a bleaching action.

3. It turns acidified potassium dichromate solution green.

4. It turns acidified potassium permanganate solution colourless.

The reaction of SO_2 with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution is used in the identification of sulphite

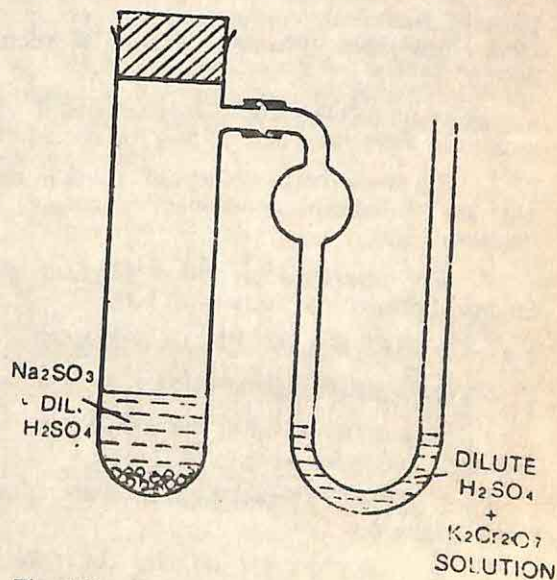


Fig. 6-24. To demonstrate the presence of sulphur dioxide ; to demonstrate the presence of sulphite ion

ion. Sodium sulphite salt is treated with dilute H_2SO_4 . SO_2 gas is evolved which is bubbled through acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution. After sometime the solution turns green indicating the presence of sulphite ion. This test also shows the presence of sulphur dioxide. If sulphur dioxide gas is bubbled through acidified solution of potassium permanganate, the purple colour of the solution disappears. This confirms the presence of sulphur dioxide and its reducing nature.

6-13-4 EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers.

1. To prepare a sample of sulphur dioxide gas (Section 6-13-1).

2. To show the presence of sulphur dioxide gas (Section 6-13-3).

3. To show the acidic behaviour of sulphur dioxide.

(Hint : Fountain experiment discussed in Section 6-7-3. Here water containing some blue litmus is used which turns red in the contact of SO_2 gas. This experiment also shows that SO_2 is soluble in water).

4. To study the reducing nature of sulphur dioxide gas (Section 6-13-2, Reducing nature ; Section 6-13-3).

5. To show its bleaching action using a piece of dyed cloth, coloured flower petals or fresh green grass. (Section 6-13-2, Bleaching action).

[Hint : Allow the moist-material to remain in the atmosphere of SO_2 for sometime].

6. To show the solubility of sulphur dioxide gas (Fountain experiment discussed in Section 6-7-3).

7. To observe some other physical and chemical properties (Section 6-13-2).

6-13-5 USES OF SULPHUR DIOXIDE

Its main uses are given below :

1. It is mainly used in the manufacture of sulphuric acid.

2. It is used in bleaching silk, wood pulp, wool, straw, etc.

3. It is used in sugar industry for refining and decolourizing sugar.

4. It is used for the manufacture of some important inorganic chemicals, e.g., sulphites, bisulphites and sulphates of sodium and calcium.

5. It is used as a germicide. It kills bacteria and fungi.

6. It is used to preserve fruits because it prevents oxidation which is responsible for destroying the fruits.

7. It is used as a disinfectant. For this purpose, doors and windows of the rooms are closed and fumigated with sulphur dioxide.

8. It can be used in refrigerators as a substitute for ammonia as it is readily liquefied.

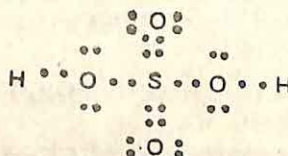
9. Liquid sulphur dioxide is used as a solvent.

6-14 SULPHURIC ACID

Molecular formula H_2SO_4

Relative molecular mass 98

Electron dot structure



Sulphuric acid is a substance of great industrial importance and the industrial prosperity of any country is fairly closely related to its sulphuric acid consumption. It is the most common oxyacid of sulphur. It is called the king of chemicals because of its extensive use in industries. Following are the key industries of India, where sulphuric acid is manufactured :

1. Hindustan Zinc Limited, Debari and Vishakapatnam

2. Hindustan Copper Limited, Khetri and Ghatsila

3. Fertilizer Corporation of India, Sindri

4. Cominco Binani Limited, Alwaye

5. DCM Chemical Works, Delhi.

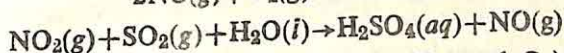
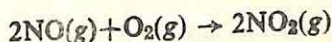
6-14-1 MANUFACTURE OF SULPHURIC ACID

Essentially, the manufacture of sulphuric acid, H_2SO_4 involves the conversion of SO_2 into SO_3 which is then processed further.

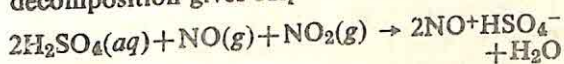
There are two main industrial processes for the manufacture of H_2SO_4 from SO_2 . *i.e.*,

1. The contact process
2. The lead chamber process

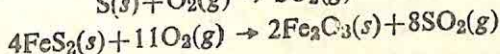
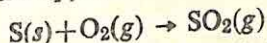
The lead chamber process is an older method for the manufacture of H_2SO_4 . In this process oxidation of SO_2 is effected catalytically by means of oxides of nitrogen in the presence of water.



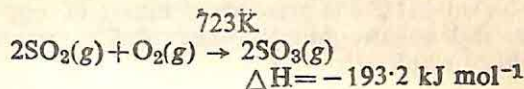
The unreacted gases (NO , NO_2 and O_2) are absorbed in H_2SO_4 and nitrosyl sulphuric acid (nitrosyl bisulphate) is formed. This on decomposition gives sulphuric acid.



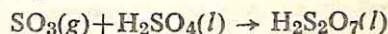
Most of the H_2SO_4 used today is produced by the *contact process* in which SO_2 is catalytically oxidized to SO_3 . SO_2 for the purpose is usually obtained by burning sulphur in air or by roasting iron pyrites.



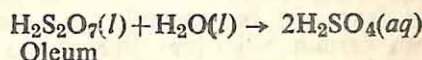
Chemical principle of the contact process. Purified SO_2 is oxidized to SO_3 catalytically (platinized asbestos or vanadium pentoxide; vanadium pentoxide is used widely which is more resistant to poisoning *i.e.* inactivation by impurities) with atmospheric oxygen at a temperature of about 723K and at atmospheric pressure. The reaction is exothermic and the temperature rises to about 873K.



The SO_3 vapours are absorbed in concentrated H_2SO_4 (98-99%) and pyrosulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$) is formed. Pyrosulphuric acid is a fuming liquid called 'Oleum'.



Water is then added to Oleum to make sulphuric acid of the desired concentration.



$$\Delta H = -69 \text{ kJ mol}^{-1}$$

Conditions for maximum yield. The oxidation of SO_2 is reversible, exothermic and proceeds with decrease in volume. The optimum conditions for a better yield in accordance to 'Le Chatelier's principle' are :

1. **Low temperature.** The oxidation of SO_2 to SO_3 is exothermic, and thus, favoured by low temperature. The reaction is too slow to be commercially feasible at low temperature. Hence, the oxidation step is carried out at about 723K. A yield of about 90% is obtained at this temperature.

2. **Use of catalyst.** This is a catalyzed reaction. The commonly employed catalysts are : platinized asbestos (spongy platinum over a base) and vanadium pentoxide.

3. **High pressure and excess of oxygen.** High pressure favours the oxidation step. However, at high pressure, the material of the plant is liable to be corroded. The reaction

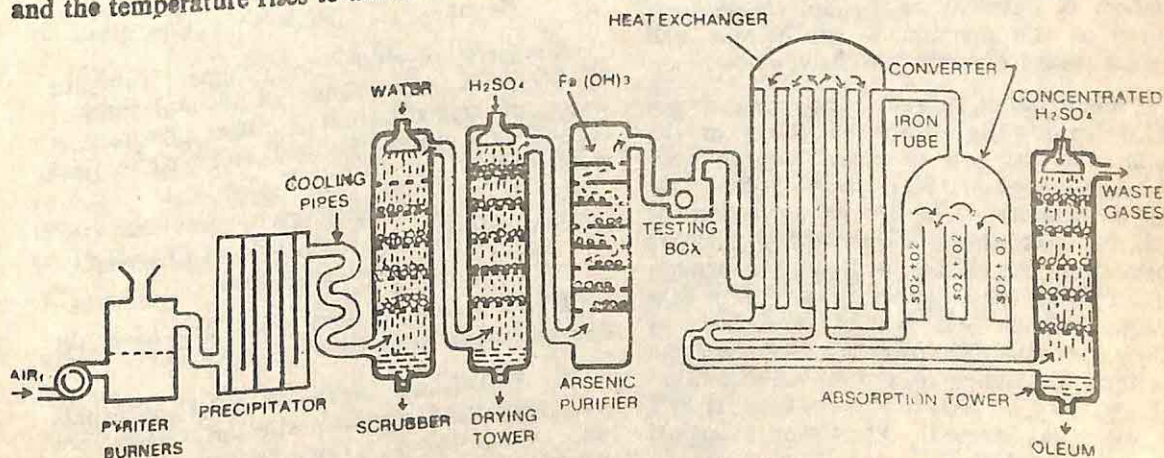


Fig. 6-25. A view of the assembly used in the contact process for the manufacture of sulphuric acid

is carried out in the presence of excess of oxygen and at atmospheric pressure for better yield of sulphur trioxide.

The integrated diagram for the manufacture of sulphuric acid by contact process is shown in Fig. 6-25. Broadly it consists of the following units :

(a) **Sulphur or pyrites burners.** Here either pure sulphur or pyrites are burnt in excess of air when sulphur dioxide is formed.

(b) **Purifying assembly.** The hot gases emanating from the burner unit are usually mixed with certain impurities like oxides of arsenic (As_2O_3), sulphur or pyrites dust particles etc. The impure hot gases are passed through a purifier which consists of an electrostatic precipitator. (Cottrell's dust electrical precipitators are much in use these days). The partially purified hot gases are then led through cooling pipes to decrease the temperature to about 375K.) They are then washed with water to remove soluble impurities. The washed gases are then dried up by a spray of concentrated sulphuric acid (dehydrating agent). The dried gases are then passed through arsenic purifier to free from arsenic impurities (arsenic oxide).

(c) **Testing box.** The purified gases are tested for any impurity by passing it through a testing box (Tyndall box).

(d) **Contact chamber or converter.** Firstly, the purified gases are heated by passing through a *preheater* (or heat exchanger) and then they are allowed to enter the converter. As they pass through the catalyst columns, they ($\text{SO}_2 + \text{O}_2$) emerge as SO_3 . After the oxidation is initiated no further heating is required as the reaction is exothermic and gases are passed directly into the chamber.

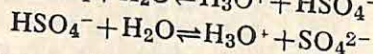
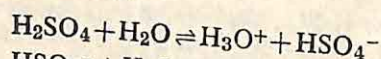
(e) **Absorption tower.** The oxidized gas (SO_3) is put into the absorption tower at the bottom from the top of which concentrated H_2SO_4 is sprayed (SO_3 gives H_2SO_4 on mixing with water. The strong attraction of the gas for water causes a layer of fog particles to form about the bubbles as they pass through water. This prevents further dissolution of SO_3 in water. Hence SO_3 is first absorbed in H_2SO_4). Here, in the tower the ascending gas reacts with descending stream of concentrated H_2SO_4 (98-99%). SO_3 is absorbed by H_2SO_4 when oleum is obtained. The tower is packed with acid-proof flint.

6-14-2 PROPERTIES OF SULPHURIC ACID

Pure sulphuric acid is a colourless oily liquid (m.p. 283.5K, b.p. 593K). It fumes when heated, due to decomposition of a small fraction of the acid into water and SO_3 . The high boiling point and viscous nature of the acid are due to the presence of partial hydrogen bonding (SO_4 groups are joined together by hydrogen bonds).

Concentrated H_2SO_4 dissolves in water with the evolution of large amount of heat. The dilution is carried out safely by pouring acid slowly into water while the solution is stirred and cooled constantly to disturb the heat of dilution.

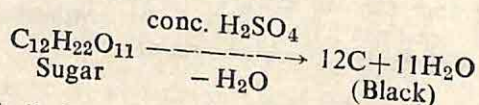
1. **Basicity.** The acid is a strong acid in aqueous solutions. It ionizes in two stages, i.e., it is dibasic.



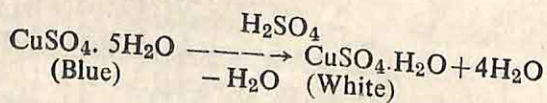
Two series of salts ($\text{M}^{2+}\text{SO}_4^{2-}$ and M^+HSO_4^-) are thus possible.

2. **Dehydrating properties.** Its strong affinity for water makes it a good dehydrating agent. Gases which do not react with the acid may be dried by passing through it. It removes water of crystallization from certain substances.

It extracts water from cane sugar and leaves behind a black residual mass.



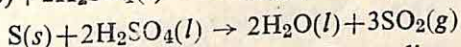
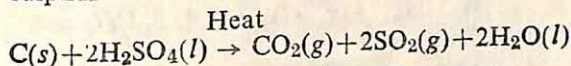
Similarly, crystals of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) lose four of its molecules of water of crystallization in the presence of concentrated sulphuric acid and a white mass is left behind.



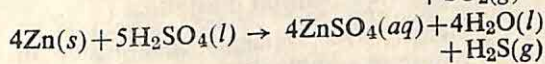
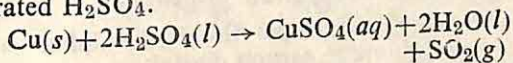
Dilute sulphuric acid does not have the dehydrating property.

3. **Oxidizing properties.** H_2SO_4 acts as an oxidizing agent, particularly when hot and concentrated. This property becomes weak on dilution.

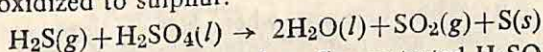
(i) **Action on non-metals.** In its reaction with non-metals, each molecule of H_2SO_4 provides one atom of nascent oxygen for oxidation purposes and is itself reduced to sulphur dioxide.



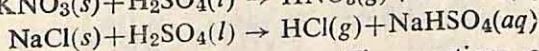
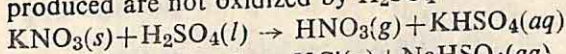
(ii) **Action on metals.** Depending upon the nature of metals, H_2SO_4 may undergo reduction to SO_2 , H_2S or S . Copper and zinc are oxidized to their sulphates by hot concentrated H_2SO_4 .



(iii) **Reaction with H_2S .** If H_2S is bubbled through concentrated H_2SO_4 it is oxidized to sulphur.

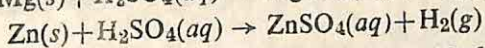
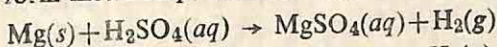


(iv) **Action on salts.** Concentrated H_2SO_4 reacts with certain salts forming acids and metal hydrogen sulphates. The acids are more volatile than H_2SO_4 itself. The acids so produced are not oxidized by H_2SO_4 .

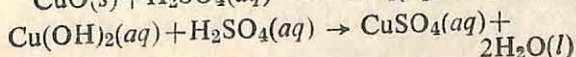
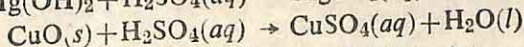
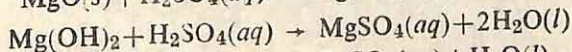
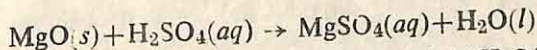
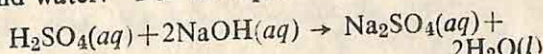


4. Acidic Properties. The reactions of concentrated H_2SO_4 are often complex due to its oxidizing action, but dilute sulphuric acid behaves as a typical acid.

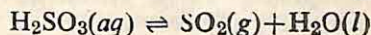
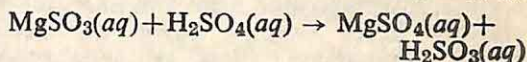
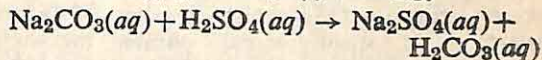
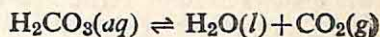
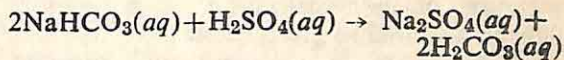
(i) **Reaction with metals above hydrogen in the electrochemical series.** Metals like Mg, Zn and iron reacts with dilute H_2SO_4 to form metal sulphates and H_2 gas.



(ii) **Reaction with bases and alkalis (metal oxides and hydroxides).** In its reaction with bases and alkalis, the acid neutralizes them and forms metal sulphates and water. For example

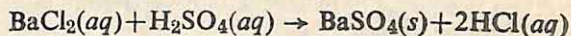


(iii) **Reaction with salts of weak acids.** In its reaction with salts of weak acids, dilute sulphuric acid forms metal sulphates and weak acids.



6-14-3 TEST FOR SULPHURIC ACID

A few ml of dilute sulphuric acid contained in a test tube is treated with a few drops of barium chloride solution. A white precipitate of BaSO_4 is formed. The precipitate is insoluble in HCl and HNO_3 .



6-14-4 EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers :

1. To prepare a dilute solution of sulphuric acid.

[Hint. Add concentrated H_2SO_4 to a large volume of water. Keep stirring the solution constantly. Also cool the solution. Never add water to sulphuric acid.)

2. To demonstrate the dehydrating properties of concentrated sulphuric acid. (Section 6-14-2. Dehydrating properties.)

[Hint. Pour a few drops of conc. H_2SO_4 over the substances kept in watch glasses. Observe the change and record your observations.]

3. To study the effect of concentrated sulphuric acid on some metals, e.g. copper turnings. (Section 6.13.1)

[Hint. Sulphur dioxide gas is evolved which can be identified (Section 6.13.3)]

4. To study the effect of dilute sulphuric acid on some metals, e.g., Zn and Mg. (Section 6.3.2)

Hint. H_2 gas is evolved which can be identified (Section 6.3.3).

6-14-5 USES OF SULPHURIC ACID

Sulphuric acid is used in various types of industries. The consumption of H_2SO_4 is a measure of industrialization of a country. Chiefly it is used as given below :

1. In the manufacture of fertilizers (ammonium sulphate and super phosphate of lime), dyes, drugs, explosives (dynamite, TNT and picric acid) disinfectants, paints, pigments, plastics, textiles (cotton wool and linen fabrics) synthetic fibres (viscose rayon and acetate rayon) photographic films, synthetic rubber, synthetic detergents and lacquers.

2. In the production of acids (HCl , HNO_3 , H_3PO_4 , etc.) diethyl ether, DDT, Na_2SO_4 , etc.

3. In the metallurgical operation of certain metals, e.g., copper, etc., (extracted from their ores using H_2SO_4).

4. For the pickling of metal surfaces (removal of oxide layer from the surface of metals) before electroplating, galvanizing, soldering or enamelling.

5. In the refining of petroleum—sulphur, tarry compounds, etc., are removed by treating crude petroleum with H_2SO_4 .

6. As laboratory reagent, dehydrating and drying agent.

7. In storage batteries used in automobiles.

8. In pharmaceuticals and for making insecticides.

9. In leather tanning industries.

WORK EXERCISES

1. Distinguish between oxygen and ozone.

2. Answer the following questions :

(i) Is ozone an isotope of oxygen ?

(ii) Is oxygen collected over water ?

(iii) Is oxygen lighter or heavier than air ?

(iv) Does oxygen act as a catalyst in the combustion process ?

(v) Does oxygen exist in the form of diatomic molecule ?

(vi) Is oxygen combustible ?

(vii) Is ozone present in the atmosphere near the earth ?

(viii) Does ozone help in preserving life on the earth ?

(ix) Is oxygen acidic or basic ?

(x) Does oxygen form basic oxide with metals ?

3. Write equations for the action of oxygen on each of the following :

H_2 , Na, Mg, Ca, C, P, S, CH_4 and NH_3

4. Answer the following questions :

(i) Is sulphur a metal or a non-metal ?

(ii) Does sulphur belong to period 3 ?

(iii) Do oxygen and sulphur show similarities in chemical properties ?

(iv) Which allotropic form of sulphur is insoluble in carbon disulphide ?

(v) Name five elements that occur in nature in combination with sulphur.

(vi) Which metal sulphide is yellow in colour ?

(vii) What happens when H_2S is bubbled through acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$?

(viii) Name the products obtained when H_2S is burnt in a limited as well as excess of air.

(ix) Is H_2S a reducing or an oxidizing agent ?

(x) Can sulphur dioxide be collected over water ?

5. (a) Why is moisture essential for sulphur dioxide to act as a bleaching agent ?

(b) Why does a piece of wood become black when concentrated sulphuric acid is dropped on it ?

(c) Oxygen and sulphur show similarities in many of their chemical properties." Comment.

(d) Why do metal sulphides occur mostly in rocks ?

6. Give reasons in one or two sentences for each of the following :

(i) Sulphur is a solid at room temperature whereas oxygen is a gas.

(ii) Both sulphur and oxygen differ in molecularity ?

(iii) Sulphur dioxide gas is collected by upward displacement of air.

(iv) Sulphur dioxide gas is not used for sterilizing water.

(v) Sulphur trioxide is the only anhydride of sulphuric acid.

7. List important sources of oxygen and sulphur.

8. (a) What are the names of the elements whose atomic numbers are 8 and 16 respectively? Give the significance of their names.

(b) Give the working principle involved in the continuous supply of H_2S gas.

9. What happens when ;

(i) $BaCl_2$ solution is treated with dilute sulphuric acid.

(ii) Copper oxide is treated with dilute sulphuric acid.

(iii) Zinc is treated with hot concentrated sulphuric acid.

(iv) Oleum is mixed with water.

(v) Sulphur dioxide is treated with hydrogen sulphide.

(vi) Hydrogen sulphide burns in oxygen.

(vii) Sulphur is treated with hot concentrated alkali.

(viii) Methane is burnt in the presence of oxygen.

(ix) Carbon disulphide is burnt in the presence of oxygen.

(x) Hydrogen sulphide is bubbled through concentrated H_2SO_4 .

10. (a) How will you get CO_2 , SO_2 , H_2S and H_2 using sulphuric acid?

(b) Suggest a method using H_2SO_4 for the preparation of the following :

(i) Na_2SO_4 (ii) HCl (iii) HNO_3 ,

(iv) $FeSO_4$

HALOGENS

(GROUP VIIA NON-METALS)

6-15 HALOGENS

Fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) are collectively known as halogens. The name halogen is derived from Greek word 'halos' which means 'sea salt former'. This reflects that most of these elements exist in sea water in the form of salts. These elements constitute group VIIA of the periodic table. Elements of group VIIA and those of groups IIIA to VIA including zero group elements belong to *p*-block of the periodic table.

Family relationship and general trends

All halogens exist as diatomic molecules at ordinary conditions. The molecules are held together by van der Waals forces (weak forces). The strength of these forces increases with increasing size of molecules. Thus, the physical state of these elements changes from gas to liquid to solid (Table 6-6). Because of the increasing van der Waals forces, the melting and boiling points of the halogens increase from fluorine to iodine.

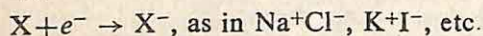
They are all coloured because they absorb light in the visible region resulting in the excitation of outer electrons to higher energy levels. The smaller the atom, more will be the energy needed for excitation. Gaseous F_2 molecules absorb high energy violet light and appear yellow while gaseous I_2 molecules absorb low energy yellow light and appear violet. Similarly, chlorine molecules appear yellowish green and bromine molecules reddish brown (Table 6-6).

Table 6-6 Description of halogens

Element	Symbol	Atomic Number	Electronic configuration					Colour and physical state
			K	L	M	N	O	
Fluorine	F	9	2	7				Pale yellow gas
Chlorine	Cl	17	2	8	7			Greenish yellow gas
Bromine	Br	35	2	8	18	7		Reddish-brown liquid
Iodine	I	53	2	8	18	18	7	Greyish black solid (violet-vapour)

The members of the family are very similar in chemical behaviour, since they have seven electrons in the valence shell. They have only one electron less than the number present in the adjacent noble gas. They can acquire a noble gas electronic configuration by :

(i) accepting one electron from a donor group, and



(halogen atoms become stable univalent ions)

(ii) forming a single covalent bond as in the halogen molecules ($X-X$) and hydrogen halides ($H-X$).

Fluorine is the most reactive of all the elements. The reactivity decreases from fluorine to iodine $F_2 > Cl_2 > Br_2 > I_2$.

6-15-1 OCCURRENCE

Halogens do not occur free in nature due to their highly reactive nature. They are generally found in combination with metals as simple halides. Table 6-7 shows the relative abundance of the halogens in nature.

Table 6-7 Abundance of halogens in nature

Element	Abundance in earth's crust (ppm)	Abundance in sea water (ppm)
Fluorine	800	8
Chlorine	400	19,000
Bromine	2	65
Iodine	0.3	Extremely small

The most reactive fluorine is found in the combined form as fluoride in rocks and in many natural water supplies. Fluorine occurs in a number of minerals, the most common being fluorapatite, CaF_2 ; cryolite, Na_3AlF_6 ; and fluorapatite, $CaF_2 \cdot 3Ca_3(PO_4)_2$.

Chlorine is mainly found as sodium chloride, $NaCl$ in sea water. It is also present in sea water with other alkali and alkaline earth chlorides. Brine wells and rock salt ($NaCl$) deposits make a rich source of chlorine.

Bromine is also found in sea water as bromides ($NaBr$, KBr , $MgBr_2$). It is also found in salt mines as sodium bromide.

Sea water is a poor source of iodine. However, sea weeds absorb some iodides from sea

water and make a good source for iodine. Chile has extensive deposits of calcium iodate which is found along with the deposits of sodium nitrate.

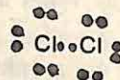
6-16 CHLORINE

Relative atomic mass 35.45

Molecular formula Cl_2

Relative molecular mass 70.90

Electron-dot structure

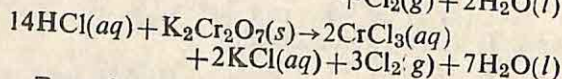
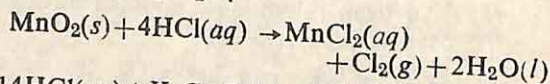


Chlorine gas was discovered by Scheele in 1774 but not recognized as an element. In 1810, Davy recognized the gas as an element and he called it chlorine (Greek, chloros = greenish yellow).

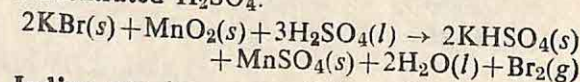
6-16-1 LABORATORY PREPARATION OF CHLORINE (ALSO BROMINE AND IODINE)

Chlorine is prepared commercially by electrolysis of concentrated aqueous sodium chloride, in which industrially important hydrogen and caustic soda are also produced.

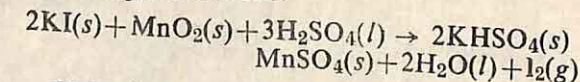
Laboratory methods for the preparation of chlorine involve oxidation of hydrochloric acid with manganese dioxide, MnO_2 or potassium dichromate, $K_2Cr_2O_7$.



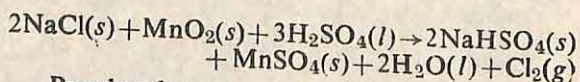
Bromine can be prepared by heating a mixture of KBr and manganese dioxide with concentrated H_2SO_4 .



Iodine can be prepared by using potassium iodide in place of KBr .



Chlorine can also be prepared by gently heating a mixture of manganese dioxide and sodium chloride with concentrated sulphuric acid.



Powdered manganese dioxide is put in a round bottomed flask and concentrated hydro-

chloric acid is added through a thistle funnel. On heating the contents, effervescence takes place and greenish-yellow chlorine gas is pro-

duced (Fig. 6-26). Traces of hydrogen chloride from the hydrochloric acid are removed by passing the gas through water ; the chlorine gas

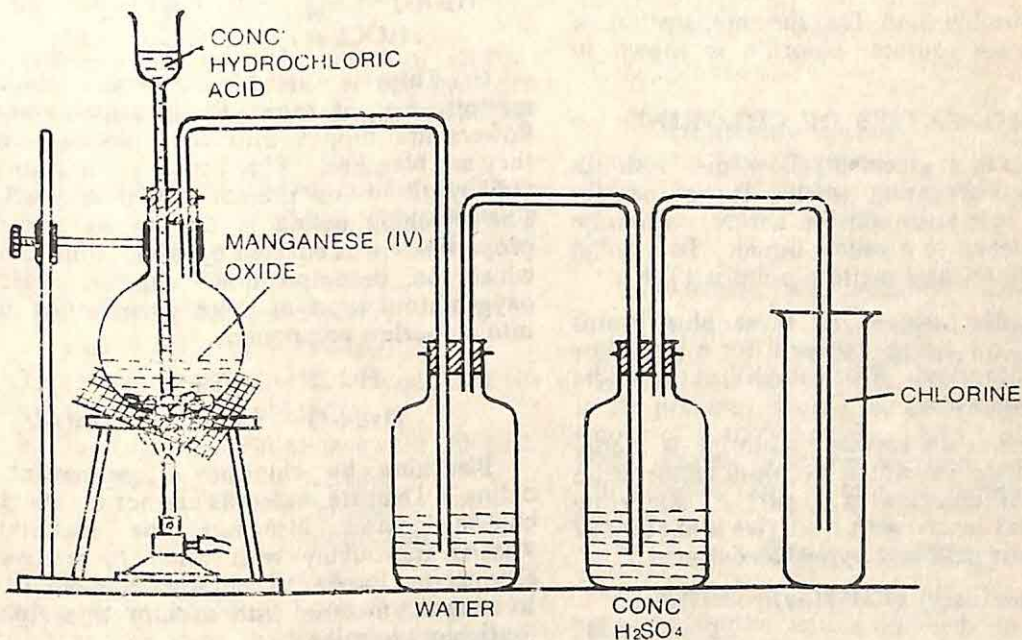


Fig. 6-26 Laboratory preparation of chlorine from hydrochloric acid

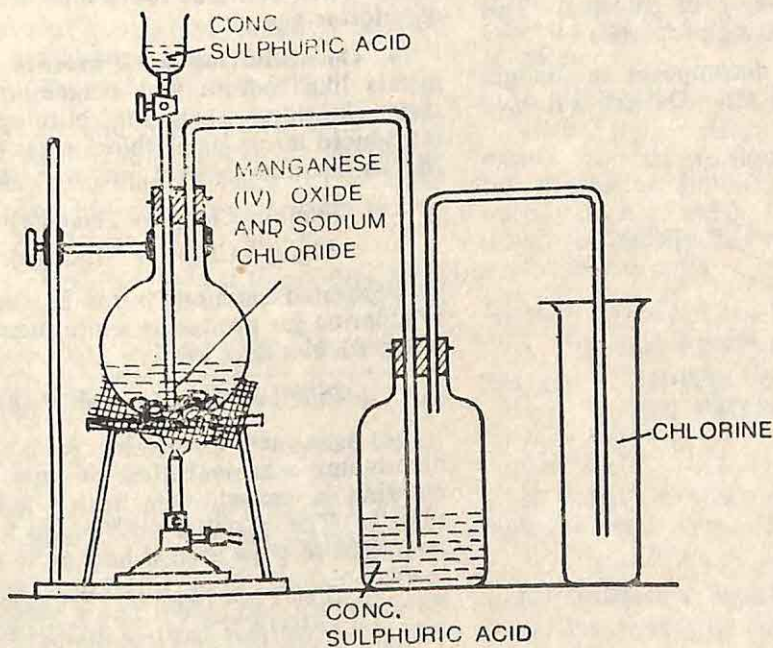


Fig. 6-27 Preparation of chlorine from sodium chloride

is then dried by bubbling through concentrated sulphuric acid and collected by upward displacement of air.

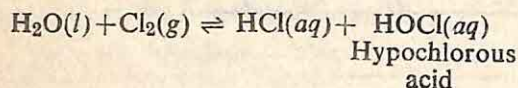
The assembly used for the preparation of chlorine from sodium chloride is shown in Fig. 6-27.

6-16-2 PROPERTIES OF CHLORINE

Chlorine is a greenish-yellow gas with an unpleasant suffocating smell. It is heavier than air. It is poisonous in nature. Chlorine can be liquefied to a yellow liquid. Its boiling point is 238.4K and melting point is 172K.

1. **Acidic nature.** It turns blue litmus red which on being exposed for a long time becomes colourless. This establishes the acidic nature of chlorine.

2. **Action on water.** Chlorine is moderately soluble in water at room temperature (3 parts of chlorine in 1 part of water by volume) and reacts with it to give a mixture of hydrochloric acid and hypochlorous acid.



The aqueous solution is yellowish-green in colour and is known as 'chlorine water'. Such a solution smells strongly of chlorine. This solution has two interesting properties :

(i) Chlorine water decomposes in sunlight to give oxygen (Fig. 6-28). Oxygen is formed

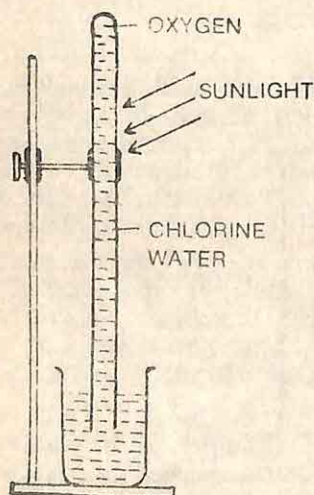
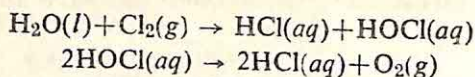
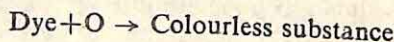
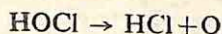


Fig. 6-28. Effect of sunlight on chlorine water.

due to the decomposition of hypochlorous acid by sunlight.



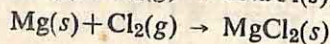
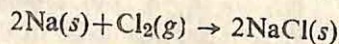
(ii) Chlorine water bleaches many colouring matters, e.g., if moist litmus paper, grass or flowers are dipped into the chlorine water, they are bleached. Blue litmus is first turned red by the acids present and then bleached. The bleaching action is due to its oxidizing properties. It is effected by hypochlorous acid which on decomposition supplies nascent oxygen atom to dyes, thereby converting them into colourless compounds.



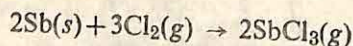
Bleaching by chlorine is permanent in nature. Delicate materials are not bleached by chlorine. After bleaching, the material is washed thoroughly with water to remove all chemicals. Excess of chlorine is removed by treating the material with sodium thiosulphate (antichlor) solution.

3. **Combustibility.** Chlorine is a non-combustible gas but it supports combustion. Many metals continue to burn in the presence of chlorine gas.

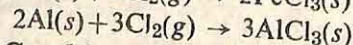
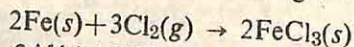
4. **Combination with metals** (a) Active metals like sodium and magnesium produce their chlorides when the burning metal is introduced into a jar of chlorine gas (Fig. 6-18). Metals continue to burn for some time.



Preheated antimony burns in the presence of chlorine gas producing white fumes of antimony trichloride.

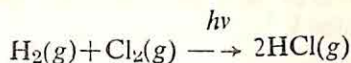


(b) Less active metals, e.g., iron and aluminium combine with chlorine when dry chlorine is passed over heated coils of the metals. The metallic coil begins to glow and continues to glow even if heating is stopped.



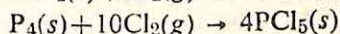
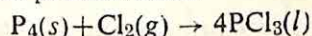
5. **Combination with non-metals.** (a) All of the halogens combine directly with hydrogen. Chlorine combines violently with

hydrogen in bright sunlight (combination is slow in diffused daylight).



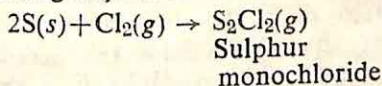
Hydrogen burning at the mouth of jet continues to burn in chlorine forming hydrogen chloride (misty fumes appear on the mouth of jar) (Fig. 6-5).

(b) Dry white phosphorus ignites spontaneously in the presence of chlorine producing white fumes of phosphorus trichloride and phosphorus pentachloride.

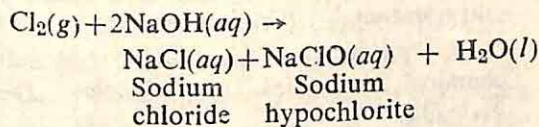


Only burning red phosphorus continues to burn in chlorine giving chlorides.

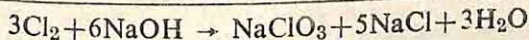
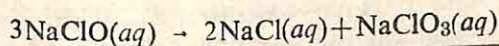
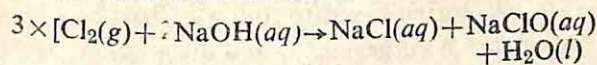
(b) Burning sulphur combines with chlorine.



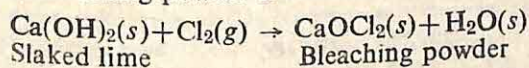
6. Reaction with alkalis. (a) In the reaction with cold and dilute solution of sodium or potassium hydroxides or a suspension of calcium hydroxide, salts of hydrochloric and hypochlorous acids are formed.



(b) With hot and concentrated solution or sodium or potassium hydroxides, a mixture of chlorate and chloride is formed. The hypochlorite is probably formed first which is converted into a chlorate and a chloride.

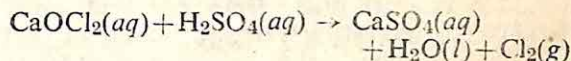


(c) When chlorine is passed over dry slaked lime, bleaching powder is formed.



Bleaching powder is used for bleaching textiles, paper, wood pulp, etc. A piece of coloured cloth, already dipped for $\sim 1/2$ hr into the suspension of bleaching powder, on treating with dilute sulphuric acid gets slowly bleached. Bleaching powder reacts with H_2SO_4

and forms chlorine which bleaches the cloth. Excess of chlorine left on the cloth is removed by dipping the piece of cloth in a solution of antichlor (NaHSO_4 or $\text{Na}_2\text{S}_2\text{O}_3$). The cloth is then finally washed with water.



7. Oxidizing nature. Chlorine is a strong oxidizing agent. It is itself reduced either to a chloride ion (by gain of electron) or to hydrogen chloride by combining with hydrogen.

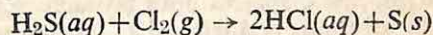
(a) **Affinity of chlorine for hydrogen**

(i) A paper (or glass wool, filter paper, etc.) soaked in hot turpentine (a hydrocarbon, $\text{C}_{10}\text{H}_{10}$) continues to burn with a reddish flame in the presence of chlorine and produces dense smoke of carbon particles. HCl is also formed which fumes in damp air and forms dense white fumes of ammonium chloride with ammonia.

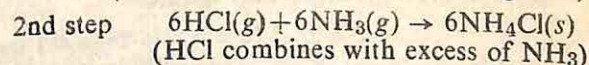
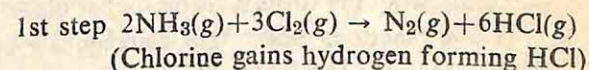


A burning wax candle also continues to burn in chlorine with a dull-red smoky flame producing much soot and hydrogen chloride.

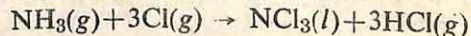
(ii) Chlorine oxidizes hydrogen sulphide to sulphur and is itself reduced to HCl . The two gases may be mixed or alternatively, chlorine may be bubbled through hydrogen sulphide solution.



(iii) If a few drops of concentrated ammonia solution is slowly added into a gas jar full of chlorine, ammonia gas from the solution burns with a greenish flame producing white clouds of ammonium chloride. The reaction occurs in two steps :



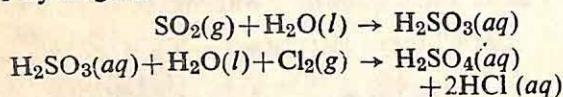
If excess of Cl_2 is used, a yellow oily explosive liquid, nitrogen trichloride is formed.



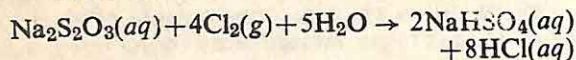
(b) **Oxidation of other compounds**

(i) **Oxidation of sulphites and thiosulphates to sulphates.** When sulphur dioxide is bubbled through water, a solution of sulphurous acid, H_2SO_3 is produced. If chlorine

is bubbled through sulphurous acid, it is oxidized to sulphuric acid (gain of oxygen) and chlorine is reduced to hydrochloric acid (gain of hydrogen).

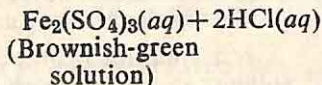
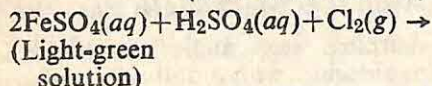
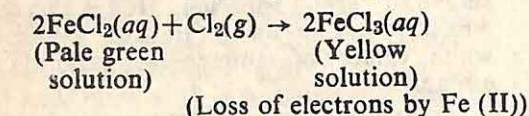


Thiosulphates are oxidized to sulphates.



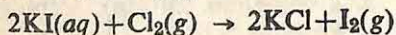
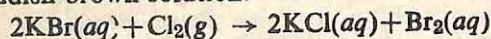
Sodium thiosulphate is used as an anti-chlor after bleaching with chlorine.

(ii) **Oxidation of iron (II) salts to iron (III) salts.** Chlorine oxidizes iron (II) chloride and acidified iron (II) sulphate to iron (III) chloride and iron (III) sulphate respectively.



(c) Displacement of halogens from their salts

Chlorine displaces both bromine and iodine from solutions of their salts. Bromine is red coloured. Hence the colourless solution of KBr turns red. Iodine makes the KI solution reddish-brown solution.



Iodine-vapours turns a starch-paper blue.

These reactions show that chlorine is more reactive than bromine and iodine.

6-16-3. TEST OF CHLORINE

All halogens can be tested by the tests given in Table 6-8.

6-16-4 EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers.

1. To prepare a sample of chlorine gas (Section 6-16-1).

2. To prepare chlorine water and establish its acidic nature.

[Hint : Chlorine is bubbled through water for long. The aqueous solution, called chlorine water is tested for its acidic nature].

3. To demonstrate the bleaching action of chlorine water (Section 6-16-2, Action on water).

4. To demonstrate the decomposition of chlorine water in sunlight. (Section 6-16-2, Action on water).

5. To demonstrate the oxidizing nature of chlorine using KBr and KI. (Section 6-16-2, Oxidizing nature ; Also Section 6-16-6).

6. To study its reaction with certain metals and non-metals (Section 6-16-2).

7. To observe some other physical and chemical properties of chlorine (Section 6-16-2).

8. To demonstrate the bleaching action of bleaching powder (Section 6-16-2 Reaction with alkalis).

6-16-5. USES OF CHLORINE

Chlorine is put to following uses :

1. As a germicide and disinfectant.
2. In the sterilization of drinking water and water in swimming pools.

Table 6-8 Detection of halogens

Property	Chlorine	Bromine	Iodine
State and colour	Greenish-yellow gas	Reddish-brown liquid	Steel grey solid
Smell	Pungent	Pungent	Pungent
Action on starch-iodide paper	Turns starch iodide paper blue	Turns starch iodide paper blue	Turns starch iodide paper violet or deep blue
Action on carbon disulphide	—	Dissolves giving orange-coloured solution	Dissolves giving violet solution

3. As a bleaching agent for substances such as cotton cloth, linen and rayon and in the paper and pulp industry.

4. As a chlorinating agent for organic compounds.

5. In the manufacture of bleaching powder, dyes, explosives, drugs, etc.

6. In the preparation of some useful plastics (*e.g.*, polyvinyl chloride, PVC) and synthetic rubbers.

7. In the preparation of some antiseptics and insecticides (*e.g.*, benzene hexachloride and DDT).

8. In metallurgical operations, *e.g.*, in recovering of gold.

9. In industries for the preparation of chemicals, *e.g.*, HCl, chloroform (an anaesthetic), sodium hypochlorite (bleaching agent) chlorates and perchlorates (used in matches, fireworks, explosives and weed killers), poisonous gas^{es} (phosgene, tear gas and mustard gas), CCl_4 (solvent), etc

10. In the manufacture of chlorine containing solvents which are used for dry cleaning.

11. As a laboratory reagent in the form of chlorine water.

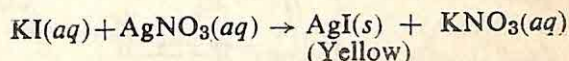
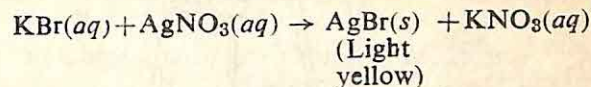
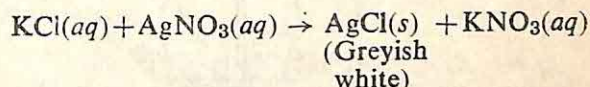
6-16-6 DETECTION OF CHLORIDE, BROMIDE AND IODIDE

Test 1. Halogens are excellent oxidizing agents. The oxidizing action of the halogens decreases in the order, $\text{F} > \text{Cl} > \text{Br} > \text{I}$. This relative power is evident in displacement reaction. The oxidizing action of chlorine is the basis of this test.

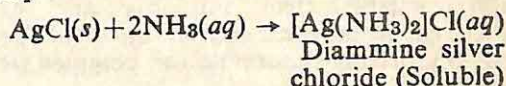
The solutions of KBr and KI are taken in test tubes marked as 'A' and 'B' respectively. A few ml of carbon disulphide (or chloroform or carbon tetrachloride) is added to each solution which becomes a lower layer. Now chlorine water is added to each solution and shaken thoroughly after closing the mouth of test tubes. Soon, tube A acquires orange (or reddish-brown) colour and tube B acquires violet colour. From the colours one can infer that bromine and iodine liberated (or displaced) from their salts by chlorine are absorbed by the carbon disulphide which forms a separate coloured layer at the bottom of each test tube.

Test 2. The colour of silver halides and their solubility in ammonium hydroxide (or aqueous ammonia) make the basis of this test.

The solutions of KCl, KBr and KI are taken in test tubes marked as 'A', 'B' and 'C' respectively. A few drops of dilute nitric acid is added to each solution. Now silver nitrate solution is added to each solution and shaken thoroughly. In each test tube precipitate of different colours appears. In tubes A, B and C, there is greyish white, light yellow and yellow precipitate respectively. Thus from the colour of the precipitates the presence of Cl^- , Br^- and I^- ions can be ascertained.



The presence of these ions is further ascertained from the solubility of silver halides in aqueous ammonia. Silver chloride is soluble in aqueous ammonia due to complex formation.



The precipitate reappears on adding dilute HNO_3 . Silver bromide is sparingly soluble in aqueous ammonia whereas silver iodide is insoluble.

6-17 HYDROGEN CHLORIDE (HYDROCHLORIC ACID)

Molecular formula	HCl
Relative molecular mass	36.45
Electron dot structure	$\begin{array}{c} \bullet \bullet \\ \text{H} \bullet \bullet \text{Cl} \bullet \bullet \\ \bullet \bullet \end{array}$

Hydrochloric acid is one of the important mineral acids and ranks along with sulphuric and nitric acid in usefulness. Traces of hydrogen chloride gas are found in volcanic gases. As chlorides, it is found in earth's crust and in sea water. Small quantities of hydrochloric acid are present in gastric juices.

6-17-1 PREPARATION OF HYDROGEN CHLORIDE

Hydrogen chloride is prepared both in the laboratory and on a commercial scale by the

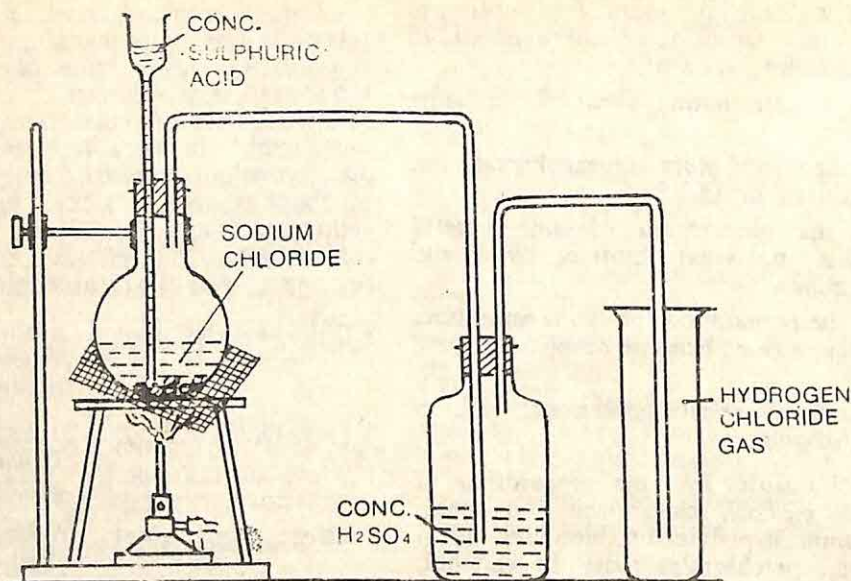
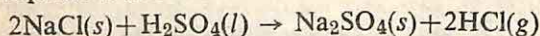


Fig. 6-29. Preparation of hydrogen chloride gas

treatment of sodium chloride with hot concentrated sulphuric acid. Hydrogen chloride is more volatile than sulphuric acid and is removed from the reaction as it is formed, thereby driving the reaction to completion.



Only at higher temperatures, than those normally attained in the laboratory the normal sulphate is formed.



The gas is collected by upward displacement of air as the gas is heavier than air (Fig. 6-29) Hydrogen chloride gas is dried by bubbling through concentrated sulphuric acid.

On a large scale, hydrogen chloride can be produced by burning chlorine in hydrogen. A large amount of hydrogen chloride is available as a by-product in the chlorination of organic compounds.

6-17-2 LABORATORY PREPARATION OF HYDROCHLORIC ACID

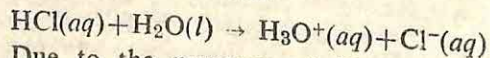
Aqueous solution of hydrogen chloride is called hydrochloric acid. A concentrated solution of hydrochloric acid (36% by weight of HCl gas) cannot be prepared simply by passing HCl gas through a delivery tube into water, since the high solubility of HCl gas would cause the water to suck back into the generating vessel (this could be disastrous, as

water would flow back into the sulphuric acid). For this purpose, a special device to prevent 'sucking back' is to use an inverted funnel as shown in Fig. 6-13. The working of the device has already been discussed under ammonia. The process is repeated until a saturated solution is obtained. Then the HCl gas just bubbles through its concentrated solution.

6-17-3. PROPERTIES OF HYDROGEN CHLORIDE

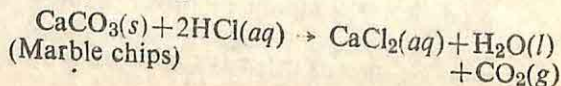
Hydrogen chloride is a colourless poisonous gas with choking smell. It is heavier than air. It is highly soluble in water. Its high solubility can be demonstrated by 'fountain experiment' in a manner similar to that for ammonia.

1. Reaction with water. When dissolved in water, hydrogen chloride solution turns blue litmus red and, hence, is acidic in nature. In aqueous solution of HCl gas H^+ and Cl^- ions exist. H^+ ions exist as $\text{H}_3\text{O}^+(aq)$ known as hydronium ion.



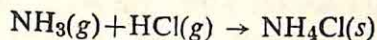
Due to the presence of $\text{H}_3\text{O}^+(aq)$ ions, hydrochloric acid exhibits all acidic properties. It conducts electricity.

It reacts with marble chips producing carbon dioxide gas.



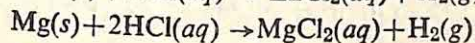
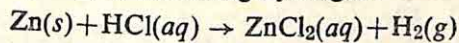
Dry hydrogen chloride gas does not turn blue litmus red. On cooling it can be liquefied. Liquid hydrogen chloride neither conducts electricity nor it reacts with marble chips. This is, because, hydrogen chloride is a covalent compound.

2. Reaction with ammonia. HCl gas gives white fumes both with NH_3 gas and aqueous ammonia.



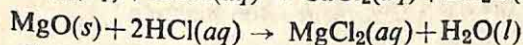
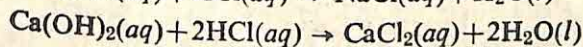
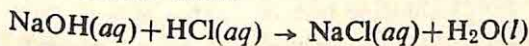
3. Acidic properties. Aqueous solution of hydrogen chloride has the usual acidic properties.

(i) Hydrochloric acid (aqueous HCl solution) reacts with metals (more electropositive than hydrogen) liberating hydrogen.

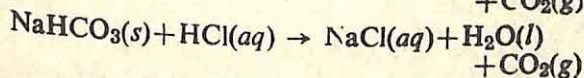
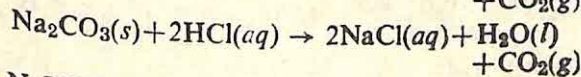
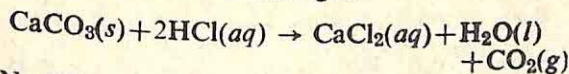


Aluminium and iron also react with $\text{HCl}(aq)$ liberating hydrogen gas. Copper (less electropositive than hydrogen) does not react liberating hydrogen gas.

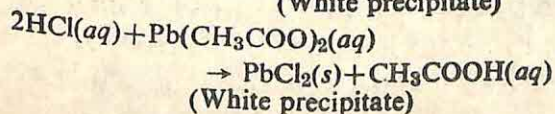
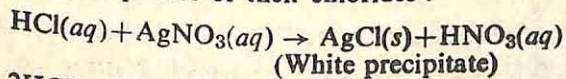
(ii) Aqueous solution of hydrogen chloride neutralizes bases (oxide and hydroxide) to form a chloride and water.



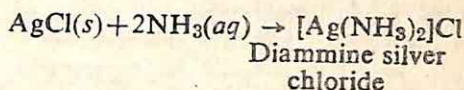
(iii) Hydrochloric acid decomposes carbonates and bicarbonates forming a chloride, water and carbon dioxide gas.



4. Precipitation reactions. With salt solution of silver, lead, etc., hydrochloric acid gives precipitates of their chlorides :

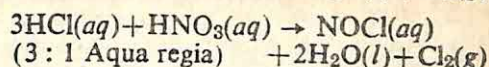
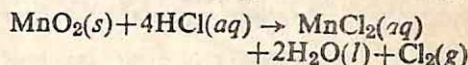
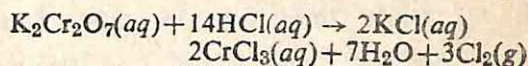
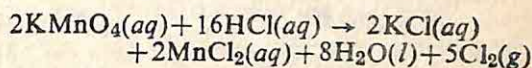


The white precipitate of AgCl dissolves in aqueous ammonia due to the complex formation.



Precipitation of AgCl is usually done in the presence of dilute HNO_3 . The precipitate does not dissolve in dilute HNO_3 . This can also be used as a test for hydrogen chloride or hydrochloric acid.

5. Reduction properties. HCl reduces some of the strong oxidizing agents and is itself oxidized to Cl_2 .



Aqua regia is used for dissolving noble metals like gold and platinum.

6-17-4 TEST FOR HYDROCHLORIC ACID

Hydrochloric acid ionizes to give $\text{H}^+(aq)$ and $\text{Cl}^-(aq)$ ions. Chloride ions help in ascertaining the presence of hydrochloric acid.

(i) It gives dense white fumes of NH_4Cl with a glass rod dipped in ammonia solution.

(ii) If dilute nitric acid, followed by AgNO_3 solution, is added to hydrochloric acid contained in a test tube, a white precipitate of AgCl is immediately formed. The white precipitate of AgCl is soluble in aqueous ammonia.

6-17-5 EXPERIMENTS

The following experiments can be performed by the students in the laboratory after receiving instructions from their class teachers.

1. To prepare a sample of hydrogen chloride gas and to demonstrate its solubility in water (Section 6-17-1) ;

(Hint. Fountain experiment discussed in Section 6-7-3).

2. To show the acidic behaviour of aqueous solution of hydrogen chloride.

(Hint. Fountain experiment discussed in Section 6-7-3. Here water containing some blue litmus is used which turns red in the contact of HCl gas. This experiment also shows that HCl is soluble in water).

3. To distinguish between dry hydrogen chloride and aqueous solution of hydrogen chloride.

(Hint. Dry hydrogen chloride does not turn blue litmus red).

4. To identify the presence of Cl^- ions in hydrochloric acid. (Section 6-17-4).

5. To study the reaction of hydrochloric acid on zinc and magnesium. (Section 6-17-3)

6-17-6 USES OF HYDROCHLORIC ACID

1. In the manufacture of chlorine by electrolysis of concentrated hydrochloric acid.

2. In the manufacture of various chlorides, dyes, drugs, paints and photographic materials. It is used in the manufacture of chloroethene, which is used in the manufacture of plastics.

3. It is used to 'pickle' iron, a process which removes rust from the surface of the metal prior to galvanization or enamelling. It is used in cleaning metals prior to electroplating.

4. It is used in the preparation of glue from bones and glucose from starch.

5. It is a constituent of aqua regia which is used to dissolve noble metals.

6. It is used as a reagent in the laboratory.

7. It is used in purification of common salts.

8. It is used in textiles, dyeing and tanning industries.

6-17-7 DISTINCTION BETWEEN NITRIC, SULPHURIC AND HYDROCHLORIC ACIDS

Tests for individual acid have been given earlier. Here some tests are given which help in identifying hydrochloric, sulphuric and nitric acids. (Table 6-9).

WORK EXERCISES

1. List the sources of halogens.

2. Give a brief account of the characteristics of halogens.

3. Give reasons for the following :

(i) Halogens are coloured in nature.

(ii) Most of the compounds formed with halogens are ionic in nature.

(iii) The reactivity of halogens decreases from fluorine to iodine, i.e., $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$.

(iv) Halogens do not occur free in nature.

(v) Pure HBr and HI cannot be prepared by the action of concentrated H_2SO_4 upon sodium bromide and sodium iodide respectively.

4. Answer the following :

(i) Is chlorine heavier than air ?

(ii) Is HCl a ionic or covalent molecule ?

(iii) Is chlorine soluble in water ?

(iv) Is chlorine an oxidizing agent ?

(v) Does red phosphorus ignite spontaneously in the presence of chlorine ?

(vi) Is chlorine used in the sterilization of drinking water ?

(vii) Is chlorine smaller in size than fluorine?

(viii) Is AgCl insoluble or soluble in aqueous ammonia ?

Table 6-9 Identification of acids

Experiments	Nitric acid	Sulphuric acid	Hydrochloric acid
Add some copper turnings	Reddish brown fumes of NO_2	—	—
Mix a few ml of barium chloride solution	—	White precipitate of BaSO_4 , insoluble in conc. HCl	—
Mix a few ml of silver nitrate solution	—	—	White precipitate of AgCl, soluble in aqueous ammonia

- (ix) Is HCl prepared in the laboratory by treating KCl with hot concentrated sulphuric acid ?
- (x) Does dry hydrogen chloride show acidic nature ?
5. What happens when :
- (i) Bleaching powder is treated with sulphuric acid.
- (ii) Chlorine is bubbled through hydrogen sulphide solution.
- (iii) Chlorine is bubbled through a solution of potassium bromide.
- (iv) Calcium carbonate is treated with dilute HCl.
- (v) Zinc is treated with dilute HCl.
6. Give the details of fountain experiment.
7. (i) Give the reactions of hydrochloric, nitric and sulphuric acids with copper turnings.
- (ii) What is aqua regia ? Give some of its reactions.
- (iii) Name the elements with atomic number 17 and 35. Give the significance of their names.
8. (i) How will you get CO_2 , Cl_2 and H_2 using hydrochloric acid.
- (ii) Suggest a method using hydrochloric acid for the preparation of the following :
- (a) NH_4Cl , (b) AgCl , and (c) Diamine silver chloride.
9. (i) Give four important uses of hydrochloric acid.
- (ii) Give four important uses of chlorine.
- (iii) Suggest the tests for chlorine and hydrochloric acid.
- (iv) Name the compound used in the manufacture of plastics.
- (v) Name the compound used as an anaesthetic.
- (vi) Name three poisonous gases which are produced from chlorine gas.
- (vii) Name two insecticides and their applications.
- (viii) Name the salt of sodium which can be used as bleaching agent.
10. Write two sentences on each of the followings :
- (i) Chlorine water, (ii) Physical states of halogens, (iii) Nature of bonds present in hydrides of halogens and compounds of halogens with alkali metals, (iv) Sea water as source of halogens, (v) Bleaching powder, and (vi) Hydrogen chloride.

KEY TERMS

6-1 Metals : Metals are elements which have a tendency to lose electrons easily to form cations. They are electropositive elements. They have characteristic lustre ; they can be hammered or rolled into sheets or drawn into wire ; they can be melted and cast into desired shapes ; they are usually good conductors of heat and electricity. Transition elements, *s*-block elements and some of the *p*-block elements are metals (Fig. 6-1). They are generally solids, one exception is mercury.

6-2 Non-metals : Non-metals are the elements which have a tendency to gain electrons to form anions. They are electronegative elements. They are not uniform in their properties. Some of them are gases ; one bromine is a liquid ; and some other are solids. Few of the non-metals have many of the characteristic properties of metals. In general, they are poor conductors of heat and electricity. They are present in the right hand region of the periodic table. They are mainly from *p*-block elements. Hydrogen is another non-metal (Fig. 6-1).

6-3 Metalloids : Metalloids are the elements which possess some of the characteristic properties of both metals and non-metals (Fig. 6-1).

6-4 Oxide : It is a binary compound of oxygen and some other element. The oxides of metals and non-metals when dissolved in water react in different ways to litmus solution. This makes the basis of classifying oxides.

- 6-5 **Acidic Oxide** : Oxides of metals generally react with water to form acidic solutions. They react with bases forming a salt, *e.g.*, P_4O_{10} , SO_2 , CO_2 , etc.
- 6-6 **Basic Oxide** : Oxides of metals generally react with water to form basic solutions. They react with acids to form a salt, *e.g.*, Na_2O , MgO , CuO , etc.
- 6-7 **Amphoteric Oxide** : Some oxides of metals show acidic as well as basic properties. They react with a strong alkali forming a salt (acidic property) and also react with an acid forming a salt (basic property), *e.g.*, ZnO , Al_2O_3 etc.
- 6-8 **Neutral Oxides** : Their solutions in water do not show acidic as well as basic properties.
- 6-9 **Acid anhydride** : A substance which on combining with water gives an acid. For example, SO_3 is the anhydride of H_2SO_4 ; N_2O_5 is the anhydride of HNO_3 ; P_2O_5 is the anhydride of H_3PO_4 . Thus an acidic oxide is called the acid anhydride of the acid it produces when it reacts with water.
- 6-10 **Oxyacid** : A compound obtained from the combination of acid anhydride and water is called oxyacid, *e.g.*, H_2SO_4 , HNO_3 , $HOCl$, etc.
- 6-11 **Hydride** : Any binary compound in which hydrogen is one of the constituents, *e.g.*, HCl , NH_3 , H_2O , etc.
- 6-12 **Deuterium** : It is the naturally occurring isotope of hydrogen having mass number 2. It may be found in water.
- 6-13 **Tritium** : It is the heaviest isotope of hydrogen having mass number 3. It is believed that tritium is produced in small amounts at high altitudes, but decomposes so rapidly that it occurs on the earth only in extremely small amounts. It is produced in nuclear reactors.
- 6-14 **Protium** : It is the most common isotope of hydrogen. Its mass number is 1.
- 6-15 **Heavy water** : It is a binary compound of deuterium and oxygen.
- 6-16 **Hydrogenation** : It is a process of adding hydrogen to an unsaturated molecule.
- 6-17 **Metallurgical operation** : It is the process of separating metals from their ores and preparing them for use.
- 6-18 **Liquefaction**. It is a term used for a process by which a gas may be liquefied by increasing the pressure on it.
- 6-19 **Fractional distillation**. It is a process by which the separation of a mixture of several liquids which have different boiling points is achieved.
- 6-20 **Fractionation**. The term is usually applied to fractional distillation.
- 6-21 **Amino acid**. A carboxylic acid which contains the amino group, $-NH_2$. These acids are the units which link together into polypeptide chains to form proteins.
- 6-22 **Proteins**. A class of complex nitrogenous organic compounds of high molecular weight which are of great importance to all living matter.
- 6-23 **Carbohydrates**. A class of compounds which are produced by plants having general formula $C_n(H_2O)_m$. *e.g.* sugar, starch, etc.
- 6-24 **Nitrides**. There are compounds of trivalent nitrogen and metals *e.g.* magnesium nitride.

- 6-25 **Lightning.** It is an electric discharge in the form of a spark or flash between two charged clouds, or between a cloud and the earth.
- 6-26 **Nitrolime.** It is calcium cyanamide.
- 6-27 **Slaked lime.** It is calcium hydroxide.
- 6-28 **Quick lime.** It is calcium oxide.
- 6-29 **Alumina.** It is the oxide of aluminium, *i.e.* Al_2O_3 .
- 6-30 **Promotor.** A compound which helps the catalyst to accelerate the rate of a chemical reaction.
- 6-31 **Solvay process.** (ammonia-soda process). It is an industrial method for the manufacture of sodium carbonate.
- 6-32 **Phosphorescence.** In the contact of air, white phosphorus glows with a greenish light. This phenomenon is known as phosphorescence.
- 6-33 **Quartz :** It is natural crystalline, silica, SiO_2 .
- 6-34 **Silicates :** It is a salt of silicic acid, H_2SiO_3 .
- 6-35 **Ultraviolet light :** It is electromagnetic radiation in the wavelength range of approximately 4×10^{-7} to 5×10^{-9} metres. Radiation from the sun, is rich in such rays.
- 6-36 **Hydrocarbons :** These are organic compounds which contain only carbon and hydrogen.
- 6-37 **Fossil :** It is the name given to the remains of an organism preserved in rocks in the earth's crust.
- 6-38 **Kipp's apparatus :** A device used in laboratories for the production of gas which is used intermittently.
- 6-39 **Hydrogen-bond :** It is a weak electrostatic chemical bond which forms between covalently bonded hydrogen atoms and a strongly electronegative atom with a lone pair of electrons (*e.g.*, oxygen, nitrogen and fluorine).
- 6-40 **Halogens.** The four elements, fluorine, chlorine, bromine and iodine having closely related and graded properties are called halogens.
- 6-41 **Van-der Waals force.** It is an attractive force existing between atoms or molecules of all substances. The force arises as a result of electrons in neighbouring atoms or molecules.
- 6-42 **Aqua regia.** It is a mixture of concentrated nitric and hydrochloric acids (1 : 3).

UNIT THROUGH EXERCISES

- 6.1. Point out the wrong statements in the following :
- (i) Metals form basic oxides, whereas non-metals form acidic oxides.
 - (ii) Hydrogen exhibits properties of a metal as well as of a non-metal.
 - (iii) Ozone is not an allotropic form of oxygen.
 - (iv) Hydrogen sulphide acts as a reducing agent.
 - (v) Dilute sulphuric acid on reacting with copper turnings gives sulphur dioxide.
 - (vi) The bleaching properties of both sulphur dioxide and chlorine depend on their reducing nature.

(vii) For the preparation of dilute sulphuric acid, sulphuric acid is added to water with constant stirring.

(viii) Nitric acid reacts with most of the metals giving similar type of products.

(ix) NH_3 gas is collected by displacement of air in an inverted bottle.

(x) Chlorine is the most active amongst halogens.

Ans. (Statements (iii), (v), (vi), (viii) and (x) are wrong.)

6-2. Name the gases produced in the following reactions :

(i) Potassium chlorate is heated in the presence of manganese dioxide.

(ii) Zinc is treated with dilute sulphuric acid.

(iii) Magnesium is treated with dilute nitric acid.

(iv) Dilute sulphuric acid is added to iron pyrites.

(v) Copper turnings are heated with concentrated sulphuric acid.

(vi) A mixture of sodium nitrite and ammonium chloride is heated.

(vii) A mixture of slaked lime and ammonium chloride is heated.

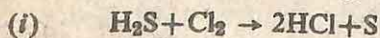
(viii) A mixture of common salt and concentrated sulphuric acid is heated.

(ix) A mixture of manganese dioxide and concentrated hydrochloric acid is heated.

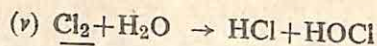
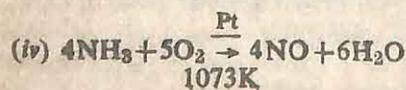
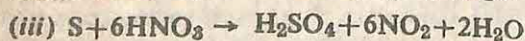
(x) Copper is treated with concentrated nitric acid.

Ans. (i) O_2 , (ii) H_2 , (iii) H_2 , (iv) H_2S , (v) SO_2 , (vi) N_2 , (vii) NH_3 , (viii) HCl , (ix) Cl_2 , (x) NO_2

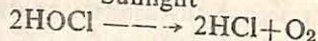
6.3. (a) Comment on the role of the substances underlined in the following reactions :



Conc. H_2SO_4



Sunlight



Ans. (i) Reducing agent (ii) Dehydrating agent (iii) Oxidizing agent (iv) Catalyst (v) Oxidizing agent

(b) Name two important allotropic forms of each of the following : phosphorus and sulphur

Ans. White phosphorus and red phosphorus; Rhombic sulphur and monoclinic sulphur.

(c) Name the element/compounds with which the following terms/processes are associated :

(i) Haber's process

(ii) Ostwald's process

(iii) Contact process

(iv) Brown ring test

(v) Kipp's apparatus

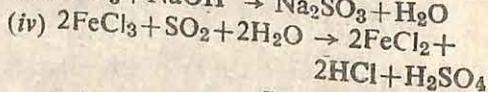
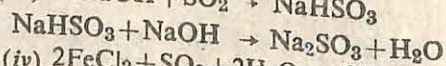
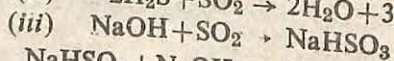
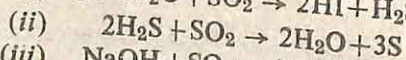
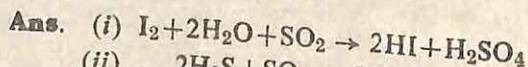
(vi) Phosphorescence

(vii) Aqua regia

(viii) Fountain experiment

Ans. (i) Manufacture of ammonia (ii) Manufacture of nitric acid (iii) Manufacture of sulphuric acid (iv) A test used in the identification of NO_3^- ion (v) For the continuous supply of H_2S gas (vi) A property of phosphorus (vii) A mixture of HNO_3 (1 part) and HCl (3 parts) (viii) Used to show the solubility of NH_3 gas and HCl gas and their basic and acidic nature respectively

6.4. (a) What happens when sulphur dioxide reacts with (i) Aqueous solution of iodine (ii) Aqueous solution of H_2S (iii) Alkali solution (iv) Aqueous solution of FeCl_3 (v) Colouring material present in flowers ? Give chemical equations.



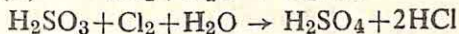
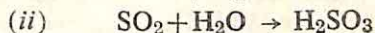
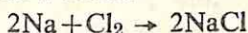
(v) Colouring matter $\xrightarrow{\text{SO}_2}$ Gets bleached

(b) What happens when Cl_2 reacts with

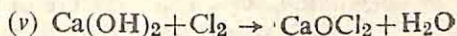
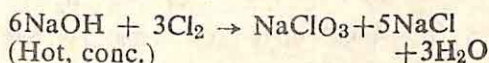
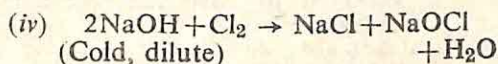
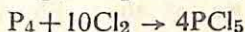
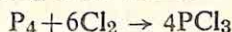
- (i) Alkali metal (ii) Sulphur dioxide solution in water (iii) A non-metal (iv) Sodium hydroxide (v) Slaked lime?

Give equations.

Ans. (i) Molten sodium burns in chlorine with a yellow flame.



(iii) White phosphorus burns spontaneously in the atmosphere of Cl_2 producing white fumes of chlorides.



(c) Write equations for the following reactions :

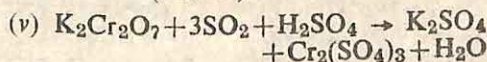
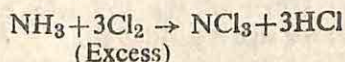
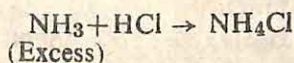
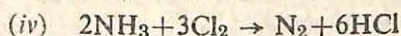
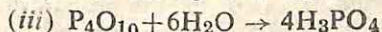
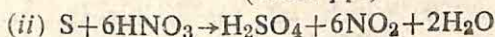
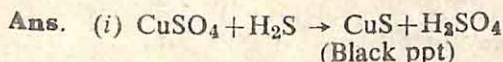
(i) H_2S gas is passed through an acidic solution of copper sulphate.

(ii) Reaction of nitric acid on sulphur

(iii) Hydrolysis of phosphorus pentoxide

(iv) Reaction of ammonia with chlorine

(v) Sulphur dioxide gas is passed through acidic potassium dichromate solution.



6.5. (a) Distinguish between hydrogen chloride and hydrochloric acid.

(b) Why is chlorine a potential disinfectant?

(c) Distinguish between the bleaching action of sulphur dioxide and chlorine.

(d) State the difference between polymorphism and allotropy.

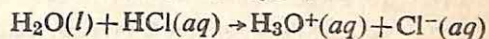
(e) Name three oxides of metals and non-metals. Give their reactions with water.

(f) What is heavy water? Why is it known as heavy water? Give its uses.

(g) Comment on the presence of oxygen and its role in atmosphere.

(h) Why is phosphorus always kept under water? Give reasons.

Ans. (a) Hydrogen chloride gas in water is called hydrochloric acid. Hydrochloric acid is present as H^+ and Cl^- ions. Here H^+ exists as H_3O^+ .



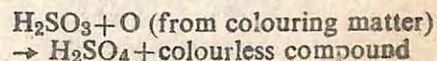
Due to the presence of H_3O^+ ions, hydrochloric acid exhibits acidic properties.

Hydrogen chloride has a single polar covalent bond. There are no H_3O^+ , H^+ or Cl^- ions. Thus, it does not exhibit acidic properties.

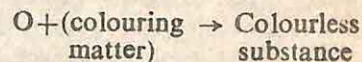
(b) Chlorine on bubbling through water produces hypochlorous acid which in turn decomposes to produce atomic oxygen, the active disinfectant, and hydrochloric acid.

(c) (i) Both sulphur dioxide and chlorine act as bleaching agents in presence of water. Dry gases do not bleach.

(ii) Bleaching by sulphur dioxide is by reduction. Oxygen is removed from the colouring matter present in the article.



Bleaching by chlorine is by oxidation when oxygen combines with the colouring matter present in the article.



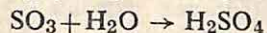
(iii) The bleaching by sulphur dioxide is temporary but the bleaching by chlorine is permanent.

- (d) When a substance (element or compound) exists in more than one form in the same physical state the phenomenon is called polymorphism. Polymorphism in an element is called allotropy. Allotropy covers all the states—liquid, solid, gas. Polymorphism is restricted to only crystalline state.

- (e) Oxides of metals and their reactions with water



Oxides of non-metals and their reactions with water



- (f) A compound of deuterium (one of the three isotopes of hydrogen) with oxygen is called heavy water (D_2O). Although it resembles water, it has a higher density at room temperature and, hence, named heavy water. It is used in nuclear reactors as a moderator for controlling the speed of fast moving electrons.

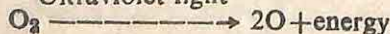
- (g) Atmospheric oxygen is continuously consumed by combustion and respiration processes. But the % of oxygen in the atmosphere remains almost constant as the oxygen is continuously reproduced by the plants by the photosynthesis process. Its percentage in the atmosphere decreases with increasing altitude. This is why mountaineers face difficulty in breathing on high mountains.

Atmospheric oxygen contains the three isotopes of oxygen: $^{16}_8\text{O}$,

$^{17}_8\text{O}$, and $^{18}_8\text{O}$. At high altitudes

(or in upper atmosphere), ultraviolet light from the sun dissociates some oxygen into atoms.

Ultraviolet light



These atoms combine with oxygen molecules forming ozone, an allotrope of oxygen. Ozone helps in preserving life on the earth by absorbing much of the harmful ultraviolet rays in sunlight.

- (i) White phosphorus is very reactive in nature. Its ignition temperature is only 308K. It spontaneously catches fire in the atmosphere and combines with oxygen forming oxide. Hence, it is always kept under water.

Multiple Choice Questions

6-6. Put a (✓) mark against the suitable choice :

- (i) Which of the following elements is expected to have the most metallic character ?
(a) P (b) S (c) Na (d) Cl
- (ii) Which of the following is wrong ?
(a) Aqua regia is a mixture of hydrochloric acid and nitric acid.
(b) Pure nitric acid does not show acidic properties.
(c) Sulphuric acid acts as an oxidizing agent in its reaction with copper.
(d) Hydrogen sulphide acts as an oxidizing agent.
- (iii) Which of the following silver halides is most soluble in ammonium hydroxide ?
(a) AgF (b) AgCl
(c) AgBr (d) AgI
- (iv) Which of the following oxidizing agents is used in the preparation of chlorine from concentrated hydrochloric acid ?
(a) MnO_2 (b) KMnO_4
(c) H_2SO_4 (d) KNO_3
- (v) Which of the following acts as reducing agent ?
(a) HCl (b) H_2SO_4
(c) HNO_3 (d) Cl_2
- (vi) Which of the following statements is wrong ?
(a) Phosphorus shows allotropy.
(b) Nitrogen is produced by heating ammonium nitrate.

- (c) Nitrogen dioxide dissolves in rain water to form nitric acid and nitrous acid.
- (d) An aqueous solution of sulphur dioxide turns starch iodide paper blue.
- (vii) Which of the following reactions is wrong ?
- (a) $\text{CuSO}_4 + \text{H}_2\text{S} \rightarrow \text{CuS} + \text{H}_2\text{SO}_4$
(Acidic solution)
- (b) $\text{NiSO}_4 + \text{H}_2\text{S} \rightarrow \text{NiS} + \text{H}_2\text{SO}_4$
(Acidic solution)
- (c) $2\text{SO}_2 + \text{O}_2 \xrightarrow[723\text{K}]{\text{V}_2\text{O}_5} 2\text{SO}_3$
- (d) $4\text{NH}_3 + 5\text{O}_2 \xrightarrow{\text{Pt}} 4\text{NO} + 6\text{H}_2\text{O}$
- (viii) Which of the following elements does not show allotropy ?
- (a) Oxygen (b) Nitrogen
- (c) Sulphur (d) Phosphorus
- (ix) Which of the following electron configurations does not represent non-metals ?
- (a) 2, 8, 7 (b) 2, 8, 5
- (c) 2, 8, 2 (d) 2, 8, 6
- (x) Which of the following statements is correct ?
- (a) Halogens are found in the combined state in the earth's crust.
- (b) Sulphuric acid is a viscous liquid.
- (c) Hydrogen sulphide gas is employed in qualitative analysis of anions and cations.
- (d) Ammonia is manufactured by Ostwald's process.
- Ans.** (i) c (ii) d (iii) b (iv) a (v) a
(vi) d (vii) b (viii) b (x) c (ix) d

6-7 Fill in the blanks :

- (i) Sulphur dioxide is collected by displacement of air.
- (ii) is used for the hydrogenation of vegetable oils.
- (iii) Substances having similar chemical properties, but different physical properties are termed
- (iv) Sulphur trioxide is the anhydride of.....
- (v) Catalyst used in the industrial preparation of sulphuric acid by contact process is
- (vi) Bleaching powder is formed when chlorine is passed through
- (vii) Chlorine is more reactive than which in turn is more reactive than
- (viii) Nitric acid oxidizes sulphur dioxide to
- (ix) reacts with in sunlight to form hydrochloric acid and oxygen.
- (x) Sulphur dioxide behaves as an oxide.

- Ans.** (i) upward (ii) hydrogen (iii) isotopes
(iv) H_2SO_4 (v) vanadium pentoxide
(vi) slaked lime (vii) bromine, iodine
(viii) sulphuric acid (ix) chlorine, water
(x) acidic.

6 8. Match the descriptions under column B against the statements given under column A.

Column A

- (i) Non-metals
- (ii) Metals
- (iii) Hydrogen
- (iv) Sulphuric acid
- (v) Nitric acid
- (vi) Chlorine
- (vii) Sulphur dioxide
- (viii) H_2S
- (ix) Calcium cyanamide
- (x) Phosphorite

Column B

- (i) Haber's process
- (ii) A dehydrating agent
- (iii) A greenish yellow gas
- (iv) Replace hydrogen from acids
- (v) Do not replace hydrogen from acids
- (vi) A fertilizer
- (vii) An oxidizing agent
- (viii) A pungent smelling gas
- (ix) A reducing agent
- (x) A source of phosphorus

REVIEW QUESTIONS

6-1 Complete and balance the following reactions :

- (i) $\text{KClO}_3 \xrightarrow{\text{Heat}}$
 (ii) $\text{I}_2 + \text{SO}_2 + \text{H}_2\text{O} \longrightarrow$
 (iii) $\text{BaCl}_2 + \text{H}_2\text{SO}_4 \longrightarrow$
 (iv) $\text{NH}_4\text{NO}_2 \xrightarrow{\text{Heat}}$
 (v) $\text{NH}_3 + \text{Cl}_2 \longrightarrow$
 (vi) $\text{NH}_4\text{OH} + \text{CuSO}_4 \longrightarrow$
 (Excess)
 (vii) $\text{Cu} + \text{HNO}_3 \longrightarrow$
 (Concentrated)
 (viii) $\text{P}_4 + 4\text{HNO}_3 \longrightarrow$
 (Concentrated)
 (ix) $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow$
 (x) $\text{NaOH} + \text{Cl}_2 \longrightarrow$
 (xi) $\text{Ca}(\text{OH})_2 + \text{Cl}_2 \longrightarrow$
 (xii) $\text{HNO}_3 + \text{H}_2\text{S} \longrightarrow$
 (xiii) $\text{NH}_3 + \text{O}_2 \longrightarrow$
 (xiv) $\text{FeS} + \text{H}_2\text{SO}_4 \longrightarrow$

6-2 (a) How do the physical properties of metals differ from those of non-metals ?

(b) Compare the metals and non-metals with respect to (i) Hydrolysis of oxides, (ii) Reaction with acids, (iii) Combination with hydrogen, and (iv) Nature of chlorides.

6-3 (i) Discuss the position of hydrogen in the periodic table.

(ii) Name the various isotopes of hydrogen with their symbols and relative atomic masses.

(iii) State the uses of hydrogen and heavy water.

6-4 (i) Justify the position of oxygen and sulphur in group VI A.

(ii) What do you understand by the term allotropy.

(iii) State the uses of oxygen.

6-5 Briefly describe the following processes :

- (a) Haber's process
 (b) Frasch's process

(c) Ostwald's process

(d) Contact process

6-6 (a) Which element is

(i) the most reactive halogen, and

(ii) with allotropic forms in group V A ?

(b) Which gas forms dense white fumes with HCl ?

(c) What is anhydride of nitric acid ?

(d) Which gas is responsible for red brown colour when nitric acid oxidizes a metal ?

(e) Which species is oxidized when H_2S is reacted with Cl_2 ?

(f) Which compound acts as a dehydrating agent in the preparation of ammonia ?

(g) Which ion gives brown ring test ?

(h) Which compound gives sulphuric acid on reacting with water in the final stages ?

(i) What would be the behaviour of pure HCl towards litmus ?

(j) At what temperature does monoclinic sulphur change into rhombic sulphur and vice-versa ?

6-7 What would happen if the hydrides of oxygen and sulphur are mixed together? How would such a solution behave towards (a) wet litmus paper, and (b) aqueous solution of lead acetate.

6-8 Explain the following :

(i) H_2S is a better reducing agent than H_2O .

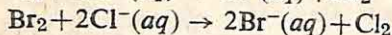
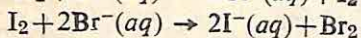
(ii) H_2SO_4 is added to water while making a dilute solution of H_2SO_4 .

(iii) The concentrated and hot H_2SO_4 is a better oxidizing agent than dilute and hot H_2SO_4 .

6-9 (a) How do you account for the high viscosity and high boiling point of concentrated H_2SO_4 ?

(b) Why does concentrated H_2SO_4 decolorize blue copper sulphate crystals ?

- (c) A measure of the industrialization of a country is the consumption of sulphuric acid. Comment.
- 6-10 Explain the following :
- In the absorption tower (contact process), water is not used for absorption of SO_3 .
 - Potassium compound is used with V_2O_5 in the contact chamber.
 - Platinized asbestos is not much in use in the manufacture of H_2SO_4 by contact process.
 - Gases are purified prior to their entry into contact chamber.
- 6-11 (a) Which properties of sulphuric acid make it useful for the industries ?
- Name the catalysts used in the manufacture of H_2SO_4 by contact process.
 - What are the various optimum conditions employed in the manufacture of H_2SO_4 by contact process ?
 - Explain the reason for the heat evolved when concentrated H_2SO_4 is added to water.
- 6-12 (i) Suggest a method using H_2SO_4 for the preparation of the following compounds :
- SO_2 ,
 - CO_2 ,
 - H_2S ,
 - HCl ,
 - H_2 ,
 - Oleum.
- (ii) Suggest a method for the preparation of oleum and Na_2SO_3 starting from SO_2 .
- 6-13 Give the electron dot structures for the following :
- H_2S
 - H_2SO_4
 - SO_3^{2-} ion
 - SO_2
 - SO_3
 - HNO_3
 - NH_3
 - HCl
- 6-14 (a) Give two natural sources of the following :
- Oxygen,
 - Ozone,
 - H_2S ,
 - SO_2 ,
 - Nitrogen,
 - Ammonia.
- (b) Give two natural sources of occurrence for each of the followings :
- Halogens
 - Phosphorus
 - Sulphur
 - Nitric acid
- 6-15 (a) How many electrons are there in the valency shell of nitrogen and chlorine ?
- How many electrons does an atom of each nitrogen and chlorine require to attain the nearest noble gas structure ?
 - What is the nature and number of bonds in nitrogen and chlorine molecules ?
 - What are the methods of detecting chlorine, bromine and iodine ?
 - Give the tests to identify chloride, bromide and iodide ions.
 - How will you distinguish between nitric, sulphuric and hydrochloric acids ?
- 6-16 Comment on each of the followings :
- NH_3 gas is collected by displacement of air in an inverted bottle.
 - Nitrogen cannot be dried over anhydrous CaCl_2 or P_2O_5 .
 - Red phosphorus does not catch fire spontaneously.
 - AgCl dissolves in aqueous ammonia.
 - Aqueous nitric acid is a strong acid.
 - Traces of nitric acid are found in rain water after lightning.
- 6-17 (a) Explain the bleaching action of chlorine. Are all the halogens capable of acting as bleaching agents ? Explain.
- (b) Give a few reactions exhibiting the relative reactivity of the halogens.
- 6-18 (a) Arrange the halogens in order of increasing :
- Atomic size,
 - Oxidizing activity,
 - Intensity of colour, and
 - Bleaching power.
- (b) Give a general method for the preparation of halogens with a chemical equation.
- (c) Give the reaction of chlorine with the following :
- Antimony
 - Wax candle
 - Turpentine, and
 - Hydrogen
- (d) Which of the following reactions will occur as given ? Suggest a generalization about which halogens will displace others from an aqueous solution of the halide ions.



6-19 (a) Suggest a method for the preparation of hydrogen chloride. Can this method be used for the preparation of hydrogen bromide and hydrogen iodide?

(b) Illustrate the behaviour of NH_3 as :

- (i) a base,
- (ii) a reducing agent, and
- (iii) a complexing agent.

(c) Starting from anhydrous sodium nitrate, suggest a method for producing nitric acid. Give its reaction with metals and non-metals.

6-20 (a) How would you prepare the following from white phosphorus :

- (i) phosphene,
 - (ii) phosphorus pentachloride,
 - (iii) phosphoric acid,
 - (iv) phosphorus pentoxide, and
 - (v) red phosphorus.
- (b) Name the constituents of phosphor-bronze and its uses.

(c) Name three nitrogenous and one phosphatic fertilizers.

(d) Name two nitrogenous explosives and two nitrogen compounds used as laboratory reagents.

(e) Name one phosphorus compound used for killing rats and in safety matches.

(f) Name a substance which can continue to burn in chlorine gas.

(g) Name one germicide and its applications.

6-21 Name the following : (i) An insecticide, (ii) A variety of plastics, (iii) Important organic chemicals obtained from chlorine, (iv) Drying agent for ammonia, (v) Catalyst used in oxidation of NH_3 , (vi) Synthetic fibres, (vii) Metals producing hydrogen with dilute HNO_3 , (viii) Fumigating substance, (ix) Compounds of sulphur used as—oxidizing agent, reducing agent and dehydrating agent, (x) Test for detecting H_2S , (xi) Bleaching agent, (xii) Reactions which prove acidic nature of H_2S , (xiii) Acid which acts as a strong oxidizing agent, (xiv) Two examples each of hydrides and chlorides of non-metals, and (xv) Isotopes of hydrogen.

UNIT 7

Some Useful Compounds



Humphry Davy
(1788-1826)

Humphry Davy, the English scientist, isolated sodium, potassium, magnesium and calcium by the electrolytic methods.

Learning Objectives.

At the completion of this unit, you should be able to :

1. Give the methods of preparations of the various compounds given in the unit.
2. Outline the properties of the compounds.
3. Recognize the uses of the compounds and thus appreciate the impact of chemistry on day-to-day life.
4. Understand the meaning of water of crystallization, slaking of lime, efflorescence, available chlorine, etc.
5. Give reasons for the bleaching action of chlorine, setting up of plaster of Paris, etc.
6. Draw outlines of the industrial units described in the text.
7. Demonstrate some of the important properties of compounds—slaking of lime, dehydration of copper sulphate, etc.

7.1. INTRODUCTION

Chemistry is one of the vital areas of science helping in the efforts of providing us with a better life. We use a large number of substances in our day-to-day life. Plastics, fuels, cosmetics, fertilizers, medicines, metals and alloys, textiles, soaps and detergents, insecticides, etc. are the boons of chemistry. They have helped in making our life comfortable.

With the above view in mind, some important chemical compounds which find their use in day-to-day life, in industries, in increasing production capacity of land, etc. have been discussed in this unit. In this unit, preparation, properties and uses of a few such substances have been discussed.

7-2 CALCIUM OXIDE, CaO

Calcium oxide is the most common and important of all the calcium compounds. Its commercial name is *quicklime* or *caustic lime*.

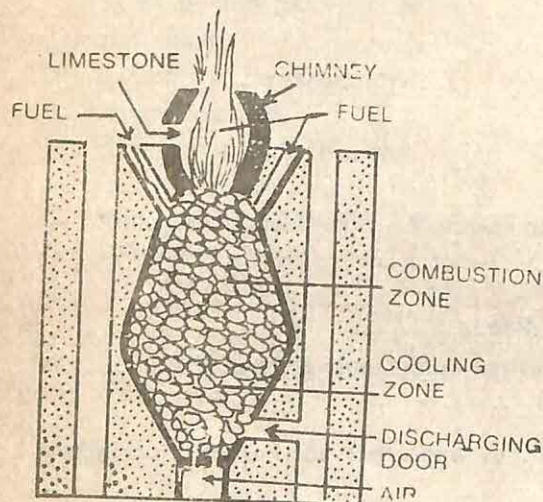
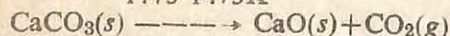


Fig. 7-1. A view of the kiln for the manufacture of calcium chloride

Preparation. Industrially calcium oxide is obtained by heating one of the forms of calcium carbonate, e.g. limestone to 1173-1473K in a lime kiln (Fig. 7.1)

1173-1473K



The thermal decomposition is reversible and thus removal of carbon dioxide prevents its recombination with calcium oxide

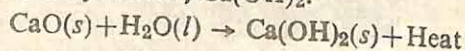
Limestone is added to the lime kiln through the hopper. Heat is provided by burning coal

in fire boxes present on the sides of the kiln. Carbon dioxide and other waste gases escape through the openings near the top. Quicklime is collected from the bottom of kiln. This is a continuous process. Quicklime is usually obtained as white lumps.

In the laboratory, calcium oxide is best prepared by heating the nitrate or hydroxide.

Properties. Pure quicklime is a white porous solid. It melts at 2850K. It is extremely stable and does not decompose even on fusion. It gives brilliant white limelight, when heated to a high temperature.

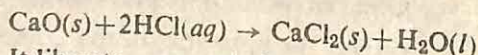
Quicklime reacts readily and violently with water at ordinary temperature (strong affinity for water). When quicklime is moistened with water, it combines with water producing a hissing sound and lot of heat. As the reaction proceeds, the mass swells and cracks, becoming very hot and steaming, finally crumbling to a fine white bulky powder. The fine powder obtained is called *slaked lime* and consists of calcium hydroxide, $\text{Ca}(\text{OH})_2$.



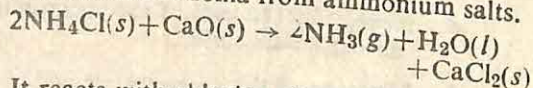
This process is called the *slaking of lime*.

In dry air, quicklime keeps indefinitely. On exposing to atmosphere for long, it absorbs moisture and carbon dioxide forming a mixture of calcium hydroxide and calcium carbonate.

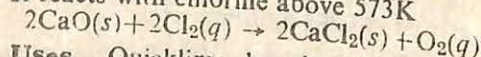
Calcium oxide is a basic oxide and dissolves in acids producing calcium salts of the acid and water.



It liberates ammonia from ammonium salts.



It reacts with chlorine above 573K



Uses. Quicklime has been put to various uses :

(i) In the manufacture of slaked lime, cement, glass, bleaching powder, calcium carbide, basic calcium nitrate, calcium bisulphite, etc.

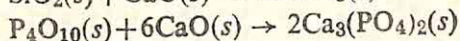
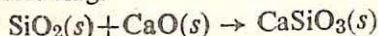
(ii) Used in the paper making, tanning, as a fertilizer and in calcium-sand mortar.

(iii) Used in the manufacture of sodalime by slaking quicklime with concentrated aqueous caustic soda.

(iv) Used in the laboratory as an absorbent for carbon dioxide and waste acidic gases and for decarboxylation of salts of carboxylic acids.

(v) Used to dry ammonia and sometimes to dry alcohol.

(vi) Used in metallurgical processes (as lining in furnaces) to remove acidic oxides as fusible slag.

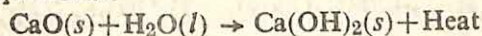


(vii) In the purification of coal gas and softening of water.

7-3 CALCIUM HYDROXIDE, $\text{Ca}(\text{OH})_2$

Calcium hydroxide is commonly known as *slaked lime* or *hydrated lime*.

Preparation. Calcium hydroxide is produced commercially by the action of cold water on quicklime.



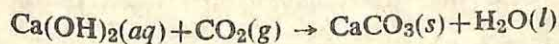
This process is known as *slaking of lime*. On adding water to a lump of quicklime, the lump begins to swell and break up. It gets very hot and some of the water is converted into steam.

It can also be prepared by the action of water on calcium metal.

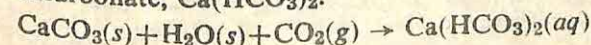
A suspension of slaked lime in water is called *milk of lime* and is used as a cheap industrial alkali. The filtered, saturated solution is called *lime water*, which is used in testing for carbon dioxide.

Properties. Calcium hydroxide is a white amorphous powder. It is slightly soluble in water and its solubility falls with increase in temperature. On heating to red heat, it rapidly evolves steam, leaving quicklime.

When carbon dioxide is passed through the saturated solution of calcium hydroxide (lime water), it first turns milky due to the formation of calcium carbonate.

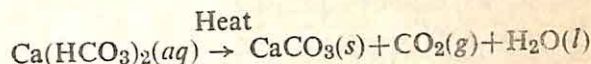


On passing CO_2 for long, the solution again becomes clear. Here excess of carbon dioxide redissolves calcium carbonate forming calcium bicarbonate, $\text{Ca}(\text{HCO}_3)_2$.

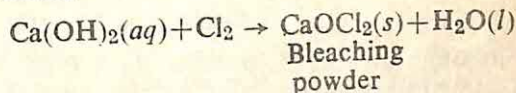


The reaction also accounts for the presence of temporary hardness in water.

When the solution of bicarbonate is heated, it acquires milkiness again due to the formation of calcium carbonate.



On passing chlorine through a cold suspension of calcium hydroxide (milk of lime), calcium oxychloride (bleaching powder) is formed.



Uses. The uses of calcium hydroxide are given as under.

1. Calcium hydroxide is used in the chemical industry, in paper making, in tanning, as a fertilizer and in lime-sand mortar.

2. Slaked lime is used in the manufacture of glass, bleaching powder, caustic soda, etc.

3. Calcium hydroxide is used for the absorption of acidic gases as in the purification of coal-gas, the recovery of ammonia from waste liquors (ammonium chloride) in the ammonia-soda process (Solvay process) and the softening of water.

4. It is commonly used in white-washing. After applying, slow absorption of carbon dioxide occurs with the formation of calcium carbonate which on drying gives a bright appearance to the surface.

5. Lime water is used in medicine as a dressing for burns and as an antidote for poisoning by sulphuric or oxalic acid.

6. Calcium hydroxide is added to soil to correct acidity and to make heavy soils lighter.

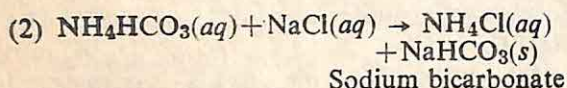
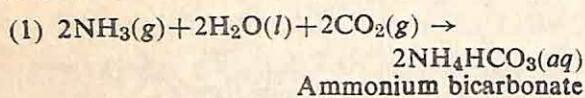
7-4 SODIUM CARBONATE, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$

Sodium carbonate is commercially known as *soda* or *washing soda*. It is available in three commercial forms :

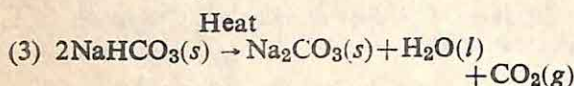
- (i) Washing soda crystals, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$
- (ii) Crystals of carbonate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$
- (iii) Soda ash, Na_2CO_3

Preparation. Sodium carbonate is manufactured by the ammonia-soda or Solvay process. This process involves the passing of carbon dioxide through a concentrated solution of sodium chloride (brine) saturated with

ammonia. NaCl gets converted into sodium carbonate. Sodium bicarbonate gets precipitated as it is less soluble in cold water. The following reactions take place :



Sodium bicarbonate, a crystalline solid is then heated to produce sodium carbonate.



Carbon dioxide and ammonium chloride obtained in the process are re-used.

The Solvay process (Fig. 7.2) involves the following stages :

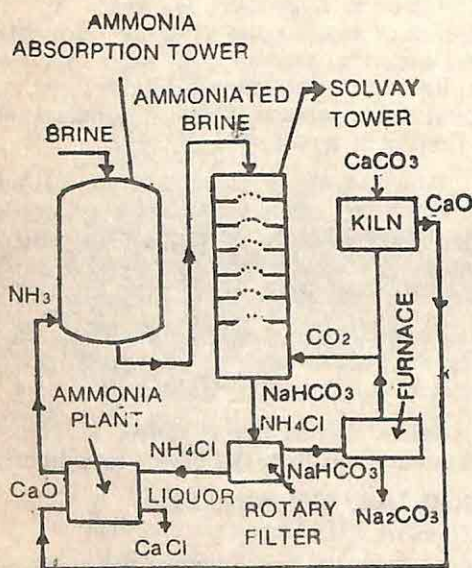


Fig. 7-2. The ammonia-soda (Solvay) process for the manufacture of sodium carbonate

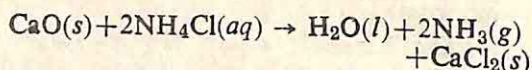
1. The preparation of ammoniacal brine. A saturated solution of common salt (brine) is passed down a tower fitted with baffle plates. Ammonia is pumped up from a bottom of the tower. Ammonia mixes with brine and saturates it.

2. The preparation of sodium bicarbonate. Carbon dioxide obtained by heating

limestone ($\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$) is blown, through the ammoniated brine passing down the Solvay tower fitted also with baffle plates. These plates ensure the thorough mixing of carbon dioxide and ammoniated brine. Here, the fundamental reactions (1) and (2) of the whole process take place to produce sodium bicarbonate.

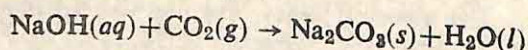
3. Formation of sodium carbonate. The sodium bicarbonate (less soluble in cold water), formed as a slurry is fed into the rotary vacuum filter, and the solid mass is then heated in furnaces to produce sodium carbonate (reaction 3). Carbon dioxide formed by the decomposition of sodium bicarbonate is passed back to the Solvay tower.

Calcium oxide obtained on heating limestone (a source of carbon dioxide) is used in the ammonia plant to reproduce the ammonia from the ammonium chloride solution.



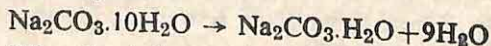
Calcium chloride is the by product of the process.

In laboratory, sodium carbonate can be prepared by passing carbon dioxide through hot concentrated solution of sodium hydroxide. Sodium hydroxide solution is saturated with carbon dioxide,

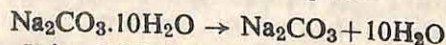


On cooling, crystals of sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) separate out. In hot medium NaHCO_3 is unstable.

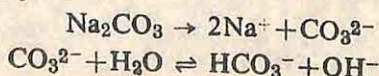
Properties. Sodium carbonate is a white crystalline substance containing water of crystallization (10 water molecules). It is efflorescent, i.e., it gives up water of crystallization to the atmosphere on standing and crumbles to powder with the composition, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the monohydrate.

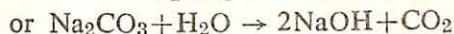
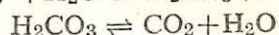


When heated strongly, it first loses all its water of crystallization and then melts at 1125K, but does not decompose.

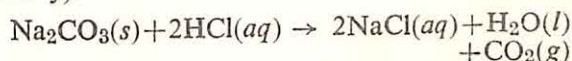


It is soluble in water with evolution of heat. The solution is alkaline in nature due to hydrolysis.

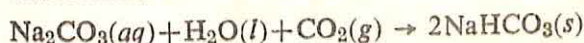




It is decomposed by acids with effervescence giving carbon dioxide (CO_2 turns lime water milky).



When carbon dioxide gas is passed through a moderately strong solution of sodium carbonate, a white precipitate of sodium bicarbonate forms.



Uses. 1. Sodium carbonate is widely used in the soap, glass, textile, paper, ceramics and food industries.

2. It is used for softening of water.

3. It is used in the manufacture of sodium hydroxide, borax, water glass and other sodium compounds.

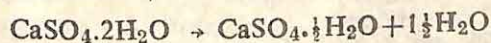
4. It is a common domestic cleansing agent.

5. It is used in the laboratory as a reagent and also as a standard base in acid-base titration.

7-5 PLASTER OF PARIS, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

The hemi-hydrate of calcium sulphate is known as 'plaster of Paris'.

Preparation. It is prepared by heating gypsum (natural source of calcium: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) at 385K. At this temperature gypsum loses 3/4th of its water



At higher temperature the anhydrous salt is formed. This is known as *dead burnt plaster*.

Properties. Plaster of Paris is a white powder. It absorbs water at ordinary temperature with evolution of heat. It has a distinct property of setting up on wetting with water. On mixing with water it sets to hard mass of the dihydrate and expands slightly.

Uses. Plaster of Paris finds uses as follows:

(i) In making casts and patterns for moulds and statues.

(ii) Used in surgery for plastering fractured parts of the body.

(iii) Used for preparing black-board chalks.

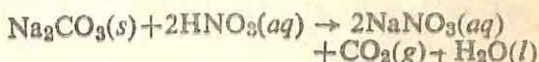
(iv) Used as fire-proofing material.

7-6 SODIUM NITRATE NaNO_3

Sodium nitrate is known as Chile saltpetre as it occurs in large quantities in a rainless desert region of Chile. It is usually found mixed with sodium iodate. Pure salt is obtained by fractional crystallization.

Preparation. (i) Natural deposits of sodium nitrate are broken into pieces and treated with water. It is separated from insoluble impurities by solution in water. The solution is evaporated by the heat of the sun. Sodium nitrate is crystallized out. It is further purified by recrystallization from water. Sodium nitrate crystallizes out first as it is less soluble than sodium iodate. The iodate bearing mother liquors are the richest source of iodine.

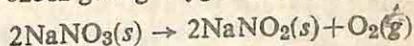
(ii) It is usually manufactured by treating soda ash with nitric acid.



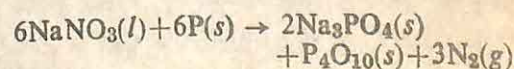
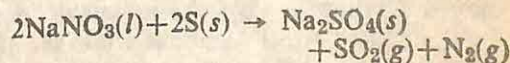
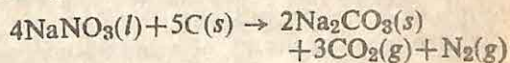
On concentrating and cooling the solution, sodium nitrate crystallizes out.

Properties. Sodium nitrate is a white crystalline solid. It is deliquescent in nature and very soluble in water.

It melts at 593K and decomposes readily above 823K giving oxygen and sodium nitrite.



A piece of glowing charcoal or feebly burning sulphur or phosphorus in the contact of molten sodium nitrate catches fire and burns explosively.



Uses. Sodium nitrate is used:

(i) As a nitrogenous fertilizer.

(ii) In the manufacture of explosives and fireworks.

(iii) In the manufacture of potassium nitrate. Potassium nitrate is used in making

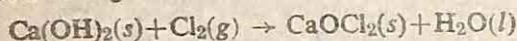
gunpowder and fireworks. Sodium nitrate is not used in gunpowder since it absorbs moisture from the air.

(iv) Also in the production of lead glass, nitric acid, sodium nitrite, etc.

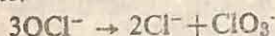
(v) For curing meat.

7-7 BLEACHING POWDER, $\text{Ca}(\text{OCl})_2$

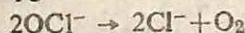
Preparation. Bleaching powder is made commercially by the action of chlorine upon slaked lime. The plant employed these days (Bechmann's plant) for the preparation is shown in Fig. 7-3.



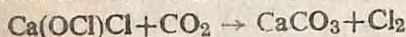
Properties. Bleaching powder, a white powder, smells strongly of chlorine. It is not completely soluble in water (lime is left behind). It is thermally unstable. It decomposes on heating. The powder also decomposes on exposure to atmosphere forming chloride and some chlorate.



The decomposition in the presence of cobalt salts gives oxygen.



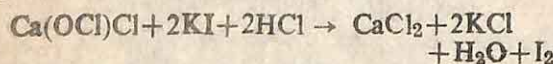
It reacts with CO_2 in the presence of moisture.



It reacts with dilute acids when the total amount of chlorine present is evolved. In the case of reaction with CO_2 , also total chlorine is evolved.

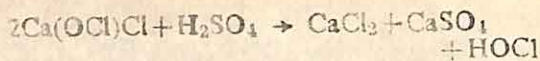


The chlorine thus released from a sample of bleaching powder on treating with dilute acid is known as *available chlorine*. Available chlorine is responsible for the bleaching and oxidizing properties of bleaching powder. The standardization of bleaching powder depends upon the amount of available chlorine. It is a powerful oxidizing agent.



The estimation of available chlorine can be done on the basis of this reaction by titrating the liberated iodine with sodium thiosulphate solution.

In the presence of a small amount of dilute acid it loses its oxygen.



Nascent oxygen causes the bleaching of the article.

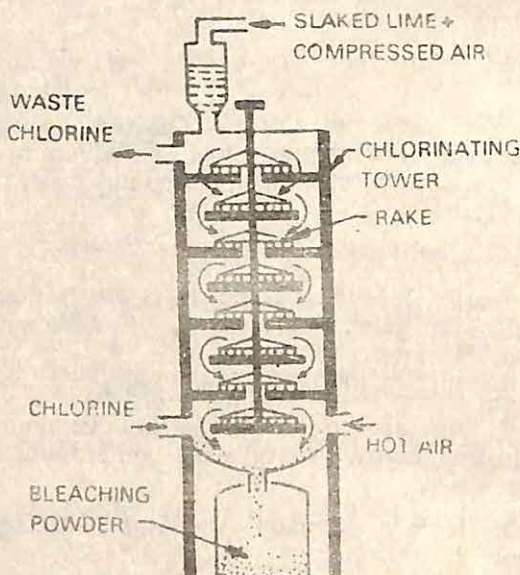


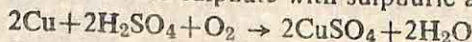
Fig. 7-3. Bachmann's plant

Uses. (i) Bleaching powder is a valuable ready source of chlorine. (ii) It is used as bleaching agent (unit 6 ; for paper-pulp, cotton and linen), disinfectant, oxidizing agent for sterilizing water (germicide) and in the manufacture of chloroform. (iii) It, along with dilute acids, renders wool unshrinkable.

7-8 COPPER SULPHATE, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

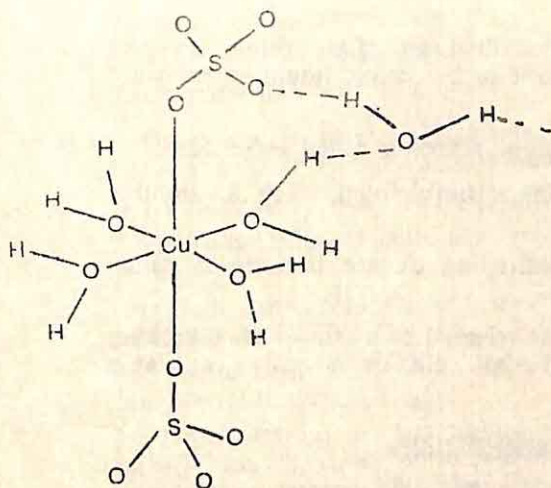
The sulphate is the most common and important of all the copper salts. On crystallization from aqueous solution, the blue pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (anhydrous salt is colourless) known as *blue vitriol* (commercial name), is formed.

Preparation. It is prepared industrially either by blowing a stream of air through scrap copper and dilute sulphuric acid or by oxidizing sulphide directly to sulphate. Sometimes sulphide is first roasted to oxide which may later be converted into sulphate with sulphuric acid.



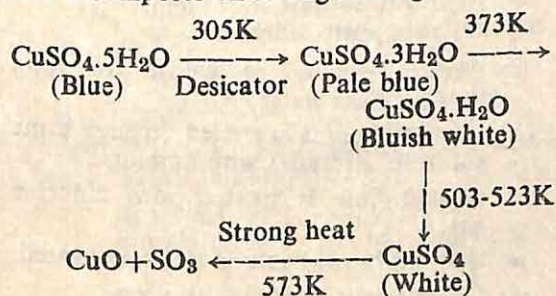
Properties. The four waters of crystallization of the pentahydrate sulphate are co-ordinated square planarly to the central copper

cation and the fifth water molecule is held by hydrogen bonds between a sulphate ion and a coordinated water molecule.



Structure of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $[\text{Cu}(\text{H}_2\text{O})_4\text{SO}_4 \cdot \text{H}_2\text{O}]$

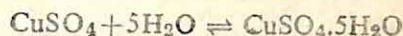
The blue crystalline pentahydrate on heating loses water in stages and finally anhydrous salt decomposes on strong heating.



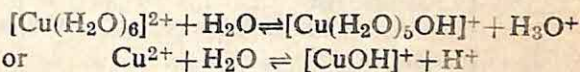
The last water molecule (attached to the SO_4^{2-} ion) is difficult to remove as it is deeply embedded in the crystal lattice.

The anhydrous salt, CuSO_4 , gets back its blue colour when treated with water. Thus, dehydration of copper sulphate is a reversible

process. This property is employed to see the presence of moisture.

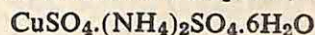


Aqueous solution of copper sulphate show acidic properties due to hydrolysis.



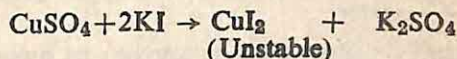
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ ions impart blue colour to the aqueous solution. Colour, however, depends on the nature of ligands (anhydrous CuSO_4 is colourless). The colour changes to dark blue when water molecules are substituted by ammonia. Thus, dark blue colour of the solution is due to $[\text{Cu}(\text{NH}_3)_4 \cdot 2\text{H}_2\text{O}]^{2+}$ ions.

It also forms double salts with alkali metal sulphate and ammonium sulphate, e.g.,



and $\text{K}_2\text{SO}_4 \cdot \text{CuSO}_4 \cdot 6\text{H}_2\text{O}$.

It reacts with iodides with liberation of iodine quantitatively. This reaction is the basis of iodometric estimation of Cu^{2+} ions.



Uses. (i) Copper sulphate is used in electroplating, in calico-printing, in dyeing, in electrotyping, in the electrolytic refining of copper, in the manufacture of pigments, as a mordant in the textile industry, in the Daniell cell and to prevent the growth of weeds in reservoirs and swimming pools. (ii) It is used as a fungicide and germicide. **Bordeaux mixtures**, a well known spray for fruit trees, is a mixture of copper sulphate and slaked lime. (iii) It is a good starting material for other compounds of copper. (iv) Anhydrous salt is employed for detecting water in liquids such as alcohol, ether, etc., and thus, used as a dehydrating agent.

KEY TERMS

7.1 Limestone. It is naturally occurring calcium carbonate.

7.2 Antidote. It is a remedy for a particular poison which generally acts chemically upon the poison; thus neutralizing it, making it insoluble, or otherwise rendering it harmless.

7.3 Antichlor. It is a substance used to remove chlorine from materials after bleaching e.g. sodium thiosulphate.

- 7.4 Efflorescence.** It is a property of some crystalline salts of losing a part of water of crystallization and becoming powdery on the surface.
- 7.5 Effervescence.** It is the escape of small gas bubbles as a result of chemical reaction.
- 7.6 Deliquescent.** It is the property of some crystalline salt of absorbing moisture from the air to such an extent as to dissolve in it or becoming liquid on exposure to air.
- 7.7 Germicide.** A substance capable of destroying bacteria is called germicide.
- 7.8 Fungicide.** A substance capable of destroying harmful fungi, such as moulds and mildews is called fungicide.
- 7.9 Disinfectant.** A substance capable of destroying disease bacteria is called disinfectant.
- 7.10 Available chlorine.** The amount of chlorine released by a sample of bleaching powder on reacting with dilute acid or carbon dioxide is called available chlorine.

UNIT THROUGH EXERCISES

7-1 Point out the wrong statements of the following :

- Quick lime has strong affinity with water.
- Calcium oxide is known as quicklime or slaked lime.
- Lime water is a clear solution of calcium hydroxide in water.
- NaCl solution is commercially known as brine.
- Soda ash is another name of washing soda.
- Solution of sodium carbonate in water is alkaline in nature.
- The dehydration of copper sulphate is a irreversible process.
- Plaster of Paris is represented by the formula, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.
- Sodium nitrate is used in gunpowder.
- The quality of bleaching powder is measured in terms of available chlorine.

Ans. Statements (iii), (v), (vii), (viii) and (x) are wrong.

7-2 With which compounds these names are associated :

- Efflorescence,
- Solvay process,
- Slaking of lime,
- Gypsum,

(v) Dead burnt plaster, and

(vi) Blue vitriol

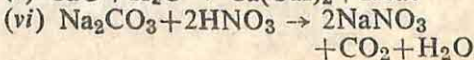
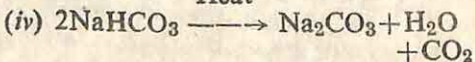
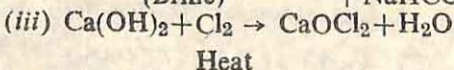
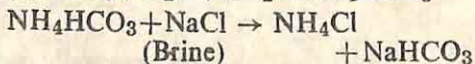
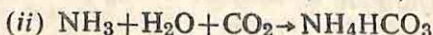
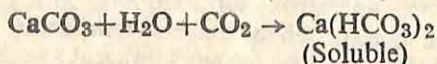
Ans. (i) Sodium carbonate, (ii) Sodium carbonate, (iii) Quicklime, (iv) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, (v) CaSC_4 , (vi) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

7-3 What happens when :

- Carbon dioxide is passed for long through lime water.
- Carbon dioxide is passed through brine solution saturated with ammonia.
- Slaked lime is treated with chlorine gas.
- Sodium bicarbonate is strongly heated.
- Quicklime is treated with water.
- Soda ash is treated with nitric acid.

Give chemical equations only.

Ans. (i) $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
(Insoluble)



7-4 Differentiate between the following sets of pairs :

- (i) Quicklime and slaked lime
- (ii) Plaster of Paris and dead burnt plaster
- (iii) Soda ash and washing soda
- (iv) Green vitriol and blue vitriol
- (v) Lime water and milk of lime

Ans. (i) Quicklime is CaO . Quicklime, on absorbing water becomes slaked lime.
 (ii) Plaster of Paris is $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. Anhydrous CaSO_4 is called dead burnt-plaster.
 (iii) Soda ash is Na_2CO_3 and washing soda is $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.
 (iv) Green vitriol is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and blue vitriol is $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
 (v) Lime water is a clear solution of slaked lime in water, whereas milk of lime is a suspension of slaked lime in water.

Multiple Choice Questions

7-5 Put a (✓) mark against the most appropriate answer.

- (i) Which of the following compounds will not work as the oxidizing agent ?
 (a) NaNO_3 (b) CaOCl_2
 (c) Na_2CO_3 (d) NaOCl
- (ii) Which of the following compounds is acidic in nature ?
 (a) Na_2CO_3 (b) CaO
 (c) $\text{Ca}(\text{OH})_2$ (d) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

(iii) Which of the following substances is produced when gypsum is heated at 385K ?

- (a) Plaster of Paris (b) Quicklime
- (c) Slacked lime (d) Calcium carbide.
- (iv) Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on heating at 373K gives
 (a) $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ (b) $\text{CuSO}_4 \cdot \text{H}_2\text{O}$
 (c) $\text{CuSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (d) CuSO_4
- (v) Sodium nitrate on heating gives :
 (a) O_2 (b) NO_2
 (c) NO (d) N_2

Ans. (i) c (ii) d (iii) a (iv) b (v) a

7-6 Fill in the blanks

- (i) Sodium nitrate occurs as
- (ii) Calcium carbonate on heating gives and
- (iii) Absorption of water by quicklime is called
- (iv) Soda ash with water gives and
- (v) The water molecules associated with copper sulphate are called
- (vi) A suspension of slaked lime in water is called

Ans. (i) Chile salt-petre (ii) CaO , CO_2
 (iii) slaking of lime (iv) NaOH , CO_2
 (v) water of crystallization
 (vi) milk of lime.

7-7 Match the statements/terms in column A with those in column B.

Column A

- (i) Caustic lime
- (ii) Copper sulphate
- (iii) Sodium nitrate
- (iv) Gypsum
- (v) Bleaching powder
- (vi) Slaked lime
- (vii) Sodium carbonate

Column B

- (i) Fertilizer
- (ii) Calcium oxide
- (iii) Plaster of Paris
- (iv) Fungicide
- (v) Nascent oxygen
- (vi) Water softener
- (vii) White-washing

REVIEW QUESTIONS

7-1 Comment on the following :

- (i) Sodium nitrate is not used in gun-powder.
- (ii) Sodium carbonate solution is alkaline in nature.
- (iii) Potassium carbonate is not manufactured by Solvay process.
- (iv) Quicklime is used as a dehydrating agent.
- (v) Plaster of Paris is widely used in hospitals.

7-2 List important uses of the following compounds :

Bleaching powder, copper sulphate and slaked lime.

7-3 Name the basic raw materials used for the preparation of :

- (a) Bleaching powder
- (b) Sodium carbonate
- (c) Potassium nitrate, and
- (d) Copper sulphate

7-4 Give a brief account of the manufacturing process of the following compounds :

- (a) Bleaching powder, and (b) Soda ash

7-5 Explain the following .

- (i) Commercial bleaching powder is sold on the basis of its available chlorine.
- (ii) Anhydrous copper sulphate is employed to detect the presence of water.
- (iii) Carbon dioxide gives white precipitate with lime water which dissolves when the gas is passed for long.
- (iv) Quicklime is used as lining in furnaces.
- (v) Soda ash is different from washing soda.

7-6 Give a brief account of the following :

- (a) Bleaching of cloth
- (b) Reaction of charcoal, sulphur and phosphorus with molten sodium nitrate
- (c) Heating of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
- (d) Solvay process
- (e) Plaster of Paris

7-7 Starting with CaCO_3 how will you prepare the following :

- (a) CaO , (b) Ca(OH)_2
- (c) Bleaching powder, and (d) CaSO_4 .

UNIT 8

Pollution and Its Effects on the Living World

Learning Objectives

At the completion of this unit, you should be able to :

1. Define pollution and pollutant.
2. Explain air pollution, water pollution and soil pollution and their effects on our health and property.
3. Describe the major sources of air pollution, water pollution and soil pollution.
4. List the common air pollutants in your locality.
5. Suggest ways to control or minimize pollution in big cities.
6. Explain that excess or careless use of fertilizers is a source of soil pollution.
7. List various water borne diseases caused by water pollution.
8. Take measures to avoid air pollution at your home.

8-1 INTRODUCTION

A new born baby is slapped on the back to begin the process of breathing that will last for a lifetime. A swimmer takes a deep breath of air before plunging into the water. All of us inhale or exhale air. Air is very essential for our survival. Occasionally, people notice that there is a foul odour in the air or that something is irritating their noses and throats. This mostly happens in large cities and around factories. In 1984, thousands of people were killed in Bhopal because of leakage of a poisonous gas from Union Carbide factory which resulted in pollution of air. Bombay tops in the discharge of vehicular traffic toxic exhaust effluent into the atmosphere in the country. Delhi comes second in the list.

Water has thousands of uses : for drinking, household purposes, agriculture etc. Certain chemicals enter the water and make it unfit for any use. Polluted water causes the water borne diseases like typhoid, cholera and dysentery. Government of India is taking all measures to stop discharging the effluents from

factories into the Ganges without treating such effluents properly.

We also require good quality of food for survival. Low grade fertilizers and water, containing certain salts, used for irrigation cause soil pollution. Food produced from such crops might prove harmful to us.

8-2 POLLUTION

Pollution is defined as combination of air, water or soil with undesirable amounts of material or heat. A substance, the presence of which causes pollution is known as *pollutant*. Heat is not a substance but still it is considered to be a pollutant. This is because even small changes in overall temperature conditions of our Earth may have disastrous effect on the quality of life. Noise pollution is also becoming serious these days in cities. It comes from aircrafts, road traffic, machinery, radios, record-players, TV, etc. In this unit we shall discuss air pollution, water pollution and soil pollution.

8-3 AIR POLLUTION

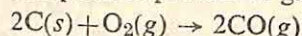
People living in large cities and around factories report about poor quality of air. Poor quality of air means presence of undesirable chemicals and substances into the atmosphere. These undesirable chemicals and substances are called air pollutants. Air pollutants reduce our enjoyment of life or affect our health and property. The quality of air varies from place to place and from time to time. Air in villages is definitely better than cities. People going for early morning walks in fields or gardens feel fresh after some time. But at noon or in the evening a large number of vehicles plying on the roads emit lots of fumes and thus air is polluted.

The concentration of gaseous pollutants are often expressed as "parts per million" (ppm) by volume. Parts per million by volume means number of molecules of pollutant present in one million molecules (1000,000 molecules) of the constituents of air. For example, 20 ppm value of CO_2 signifies that 20 molecules of CO_2 are present in one million molecules of the constituents of air.

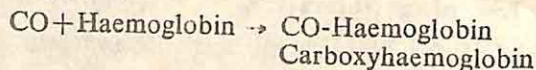
The air pollutants usually originate from industries, motor vehicles and thermoelectric power plants. Let us now consider some major air pollutants.

Carbon monoxide

The main source of carbon monoxide is the incomplete combustion by motor vehicles of carbon compounds present in gasoline.



Carbon monoxide is a colourless, odourless and very toxic gas. It is a dangerous air pollutant. Carbon monoxide combines with haemoglobin (red pigment present in blood) and produces the stable compound carboxyhaemoglobin.



Haemoglobin is needed to combine with oxygen and supply oxygen to the cells. When CO combines with haemoglobin, the amount of haemoglobin available to combine with and transporting O_2 decreases. At high CO concentrations, oxygen starvation can occur because haemoglobin is not available for combining with O_2 molecules. The result can be dizziness or death.

Carbon dioxide

Carbon dioxide is a normal constituent of air but excess of carbon dioxide is considered a pollutant. Increasing amount of CO_2 would increase the temperature on the Earth. This

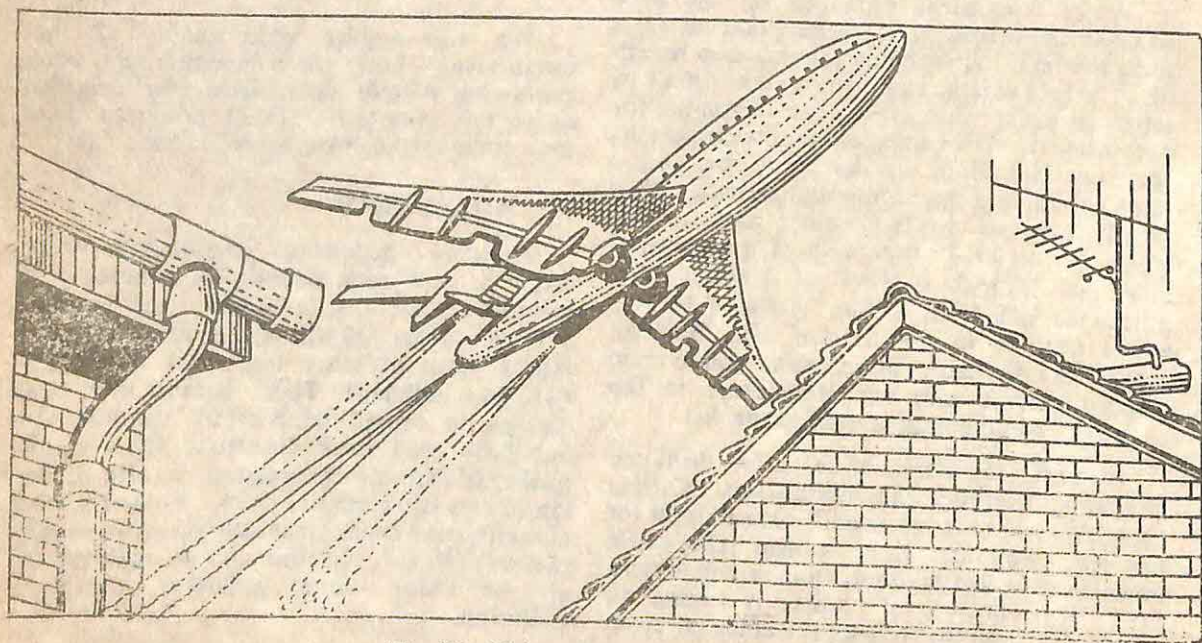


Fig. 8-1 Noise pollution from the aeroplane

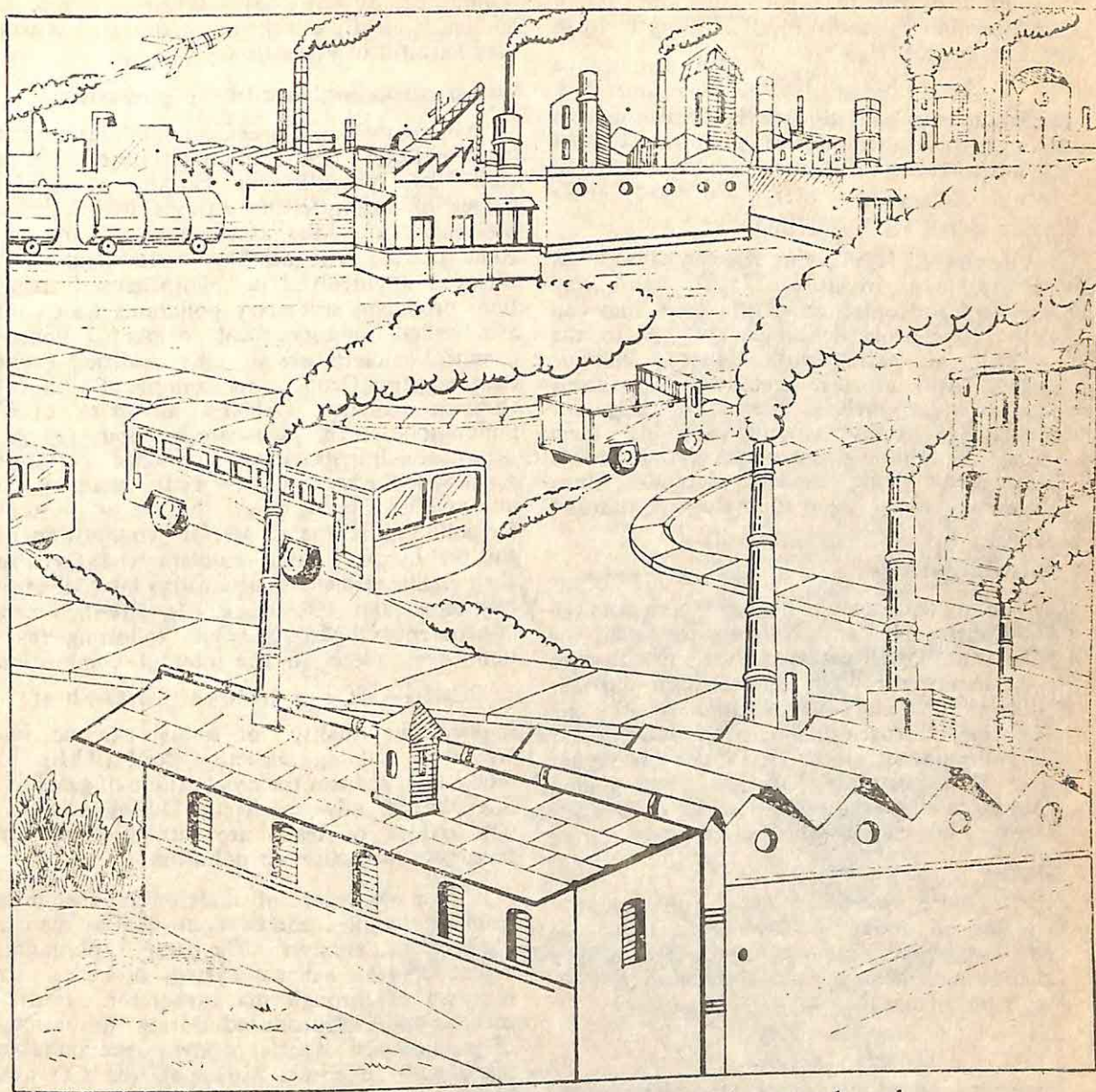
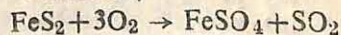
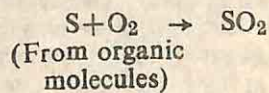


Fig. 8-2 Air pollution from (a) Factories with chimney giving out smoke, and
(b) Internal combustion engines

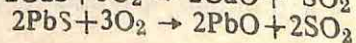
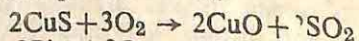
may have a serious effect on the world's climate. Glaciers may start melting and thereby flooding the coastal plains.

Sulphur dioxide

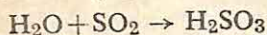
Sulphur dioxide is also a dangerous gaseous pollutant. It is formed when sulphur in the organic molecules or in FeS_2 (iron pyrites) combines with oxygen to yield SO_2 .



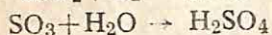
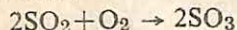
Roasting of metallic sulphide ores like CuS and PbS also produces SO_2 .



Sulphur dioxide that enters the atmosphere either combines with droplets of water to form sulphurous acid (H_2SO_3).



or can undergo oxidation to SO_3 which in turn can combine with water to yield droplets of sulphuric acid.



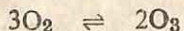
Droplets of H_2SO_4 and SO_2 can cause nose, eye and lung irritation. If SO_2 and very small H_2SO_4 droplets enter the lungs, they can cause bronchoconstriction—a decrease in the size of the air passages in the lungs. Sulphur dioxide easily attacks vegetation. The green pigment chlorophyll is affected by SO_2 and this damage causes many leaves to lose their colour. Sulphuric acid droplets corrode metals and destroy living tissues. Vegetable fibres like cotton, linen, rayon and nylon are attacked by SO_2 .

Nitrogen oxides

Among the oxides of nitrogen present in the atmosphere, NO and NO_2 are the main air pollutants. Power plants and various industries produce nitrogen oxide and nitrogen dioxide. Nitrogen oxide is converted into NO_2 by air oxidation. Nitrogen dioxide is a reddish-brown gas with pungent smell. Its toxicity is higher than NO . Breathing of NO_2 causes lung congestion and even death. It can be detected at a very low concentration i.e., 0.1 ppm.

Ozone

In nature, ozone is found in stratosphere—a region at about 24 kilometres above the Earth's surface. Ozone is formed from oxygen in the atmosphere by the absorption of ultra-violet rays from the sun.



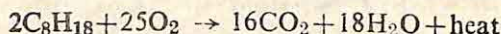
Oxygen Ozone

ozone layer does not allow ultra-violet radiations to reach the surface of the Earth and thus it protects the inhabitants of the Earth from this high energy radiations. Ultra-violet radiations destroy the organic molecules necessary for life. The exhaust fumes from supersonic aircrafts flying at high altitudes decompose ozone and thus ozone layer is damaged. The decrease in concentration of ozone in stratosphere may prove harmful for all of us. Small amount of ozone in the air around us causes eye, nose and throat irritation. People with

respiratory ailments are severely affected. Rubber is greatly attacked by ozone. It is also very harmful to vegetation.

Combustion engine and air pollution

Among moving sources, automobiles are the major polluter. Cars, buses and other vehicles emit large quantities of carbon monoxide, oxides of nitrogen and various hydrocarbon molecules into the atmosphere. In the air, some of the hydrocarbons and oxides of nitrogen are involved in photochemical reactions producing secondary pollutants which are also called photochemical oxidants. Photochemical oxidants are stronger oxidizing agent than oxygen. Ozone is an example of a photochemical oxidant. Oxidants mix with other pollutants to form *photochemical smog* (smoke + fog), which irritates eyes and lungs. Petrol or gasoline is the most common fuel used by the automobiles. In big cities, the major cause of air pollution is the incomplete combustion of this fuel by cars, buses, scooters, trucks, etc. in their engines which are also called internal combustion engines. Octanes (C_8H_{18}) are the major constituents of gasoline. The following reaction takes place in the internal combustion



engine. The quality of a fuel can be improved by adding tetraethyl lead (TEL) to the fuel. It reduces the combustion of gasoline. But it has an adverse effect. During combustion oxides of lead are formed which are poisonous and cause air pollution.

The emission of undesirable chemicals from automobiles can be controlled by the use of an exhaust catalyst. The catalyst (platinum) is placed in the exhaust system of a car. Air is drawn in through the carburetor. Hydrocarbons and CO produced during the burning of gasoline pass over the catalyst; reaction takes place with oxygen. Most of the CO and hydrocarbon molecules are converted into CO_2 and H_2O .

8-4 WATER POLLUTION

Like air, man also needs water for its survival. Good quality of water is needed for drinking and innumerable other purposes. But the activities of human beings can adversely affect the quality of water. Industrial and municipal wastes are discharged into rivers and oceans; agricultural wastes from animals, crops and fertilizers enter rivers and streams;

and rain washes air pollutants into water. The materials discharged into water are referred to as *effluents*. These effluents mixed with water resources cause water pollution.

There are two main sources that are causing water pollution seriously these days :

1. Industrial wastes. The chemical industry produces thousands of chemicals, including solvents, pesticides, detergents, acids,

bases, metals and lubricating oils. These chemicals have many adverse effects on human beings, animals and plants. Some metals can induce a variety of defects in the living system. For example, blue-grey discolouration of the skin is due to the presence of silver. Lead and cadmium metals produce cardio-vascular disorders. Polluted water is harmful for fish and other aquatic life.

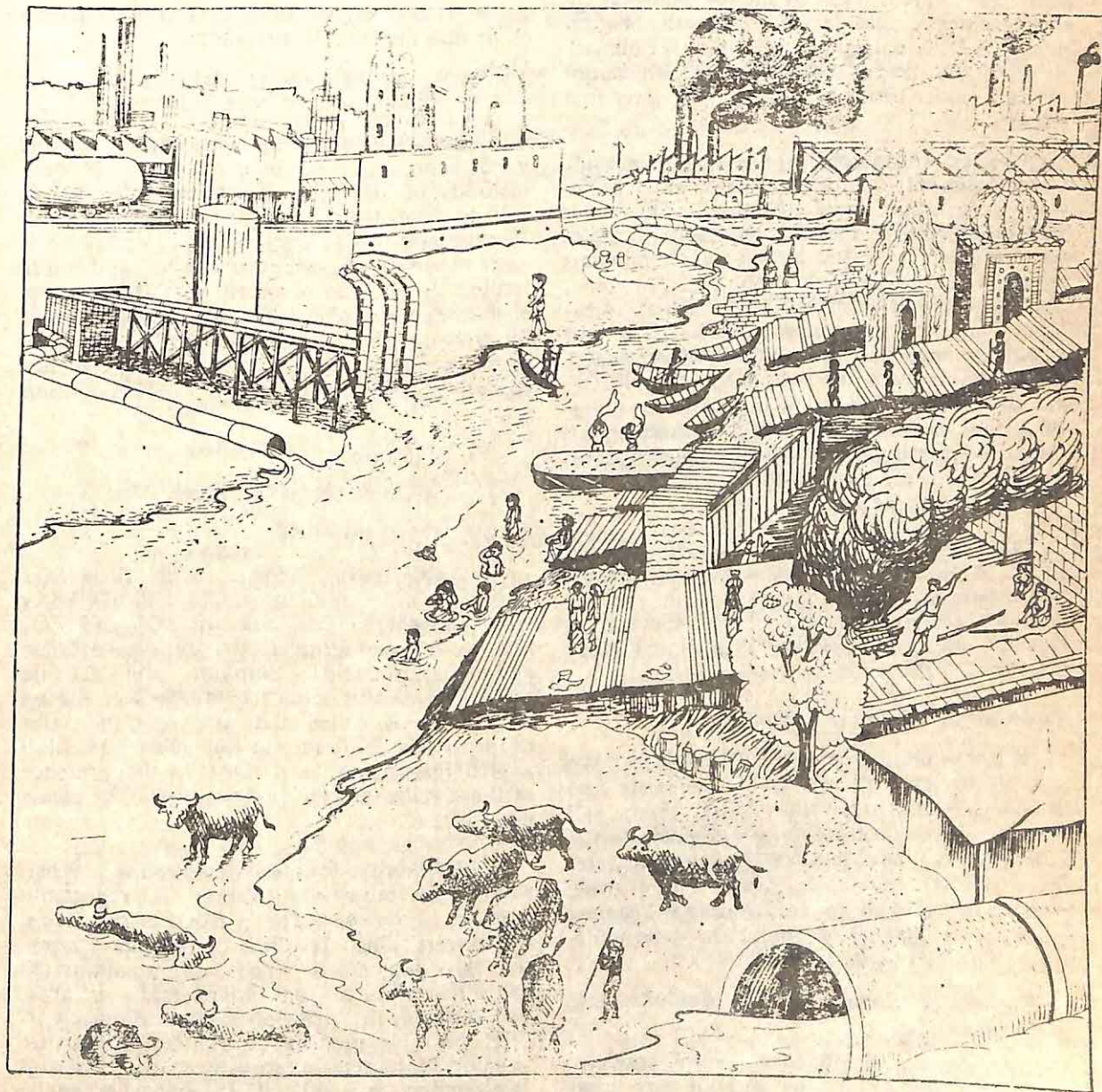


Fig. 8-3. Water pollution from industrial waste

2. Sewage disposal. Sewage contains mainly organic matters, excess phosphates, nitrogen compounds and suspended solids. Organic material in the sewage is decomposed by various micro-organisms and for this process they require O_2 . The amount of oxygen needed by bacteria in order to decompose organic material is known as *biochemical oxygen demand* (B.O.D). Quantitatively, the B.O.D is the amount of oxygen, in milligrams per litre or parts per million, used by micro-organisms to consume decomposable material in the sewage. A high B.O.D. indicates that water is polluted. At a reduced oxygen concentration, fish cannot survive, water becomes cloudy and gives foul odour.

We have discussed above the man-made water pollution. Another type of water pollution is 'Natural water pollution.' The water in lakes and rivers contains inert solid particles like soil particles, sand and insoluble minerals which are washed into water from mining, construction and other activities. These substances are not decomposed by bacteria and remain suspended or sink to the bottom. Water also contains gases like H_2S , SO_2 , CO_2 , N_2 , O_2 , etc. dissolved in it from the atmosphere. Other impurities in water are living organisms and their decomposition products like algae, diatom, bacteria, viruses, etc. which are washed into water from its surroundings.

One of the most serious cause of pollution of seas is oil. This oil comes from large ships called tankers. When it escapes into the sea it causes seabirds to die. It also spreads on beaches, and thus spoiling them for holiday makers.

Prevention of water pollution

We have limited useable water with us. We also know that all kinds of chemicals and wastes are discharged into lakes, rivers and oceans. If we keep polluting our water, future generation will have less and less useable water for drinking, producing drugs and growing crops. In recognition to this fact it becomes necessary to prevent or minimize water pollution. This can be done by :

(1) Sewage should not be dumped into rivers, directly.

(2) Industrial effluents should not be allowed to mix with water without any treatment.

(3) Use of excess fertilizers should be avoided because nitrate, phosphate salts present in fertilizers are washed into rivers and lakes.

Pollutants are removed from water in several ways. The actual treatments depend upon the types of wastes present. The polluted water is treated first to remove most of the solid insoluble material by using mechanical and chemical means. Secondly the B.O.D. of wastes is lowered by allowing aerobic bacteria to oxidize degradable material.

8-5 SOIL POLLUTION

Like air and water, we also need food for our survival. Increasing population of the world is becoming a major problem. Modern methods of intensive agriculture have helped men to meet their increasing demand of food. Use of good quality fertilizers and chemicals is very essential to make soil more and more fertile. It has been observed that excessive use of fertilizers and chemicals has made soil unfit for growing crops. This leads to deterioration in the condition of soil. This is called *soil pollution*. The main sources of soil pollution are :

- (1) Acid rain
- (2) Excessive use of fertilizers
- (3) Use of insecticide

1. Acid rain. When fossil fuels are burned, a large amount of CO_2 and SO_2 enter the atmosphere. The gaseous CO_2 and SO_2 dissolve in water droplets to produce carbonic and sulphuric acids. Sulphuric and carbonic acids are removed from the atmosphere during rain. This is called acid rain. pH of water drops to 4 or 5. Acid rain can affect vegetation and building materials. Due to the presence of these acids the soil becomes toxic for plants growth.

2. Excessive use of fertilizers. When sodium or potassium nitrate is repeatedly used as a fertilizer for getting better crops, the nitrate ions are used up by the successive growing crops. The soil is ultimately left with Na^+ or K^+ ions which make it alkaline and unfit for growing crops. Similarly, if $(NH_4)_2SO_4$ is used in excess, NH_4^+ ions are used up by successive growing crops. The soil is ultimately left with SO_4^{2-} ions which make it acidic and unfit for growing crops.

3. Use of insecticides and herbicides. Insecticides and herbicides are poisonous chemicals. They are sprayed on standing crops to kill insects, fungi, rodents, etc. These chemicals may enter the living tissues of the growing plant and accumulate in the grains or fruits. When we eat such grains or fruits,

these chemicals would enter in our body and may damage our health.

Chemicals like calcium carbide are used for ripening of fruits like bananas and mangoes. Fruits and even grains may have some chemicals on their outer surface. So it is always advisable to wash fruits, vegetables, grains, etc. with water before eating them.

KEY TERMS

- 8-1 **Pollution.** The presence of matter or heat whose nature, location or quantity produces undesired environmental effects.
- 8-2 **Pollutant.** It is a substance, the presence of which causes pollution.
- 8-3 **Air pollution.** The presence of contaminants in the air that affect our health and property.
- 8-4 **Water pollution.** The addition of sewage or industrial wastes to water and thus making it unfit for any use.
- 8-5 **Soil pollution.** Excessive use of fertilizers and pesticides that makes soil unfit for growing crops.
- 8-6 **Parts per million (ppm).** The unit commonly used to represent pollutant concentration where the concentrations are small.
- 8-7 **Smog (Smoke-fog).** Air pollution particularly associated with oxidants.
- 8-8 **Oxidant.** Any oxygen containing substance that reacts chemically in the air to produce new substances.
- 8-9 **Atmosphere.** The layer of air surrounding the Earth.
- 8-10 **Ozone.** A pungent, colourless, toxic gas. It is a major air pollutant.
- 8-11 **Sewage.** The total of organic waste and waste water generated by residential and commercial establishments.
- 8-12 **Waste water.** Water carrying wastes from homes, business and industries.

UNIT THROUGH EXERCISES

8-1. Which of the followings cause air pollution, water pollution or soil pollution?

1. Insecticides
2. Ozone
3. Sewage
4. Carbon monoxide
5. Acid rain
6. Industrial waste
7. Chemical fertilizers
8. Sulphur dioxide

9. Synthetic detergents

10. Herbicides

Ans. Air pollution : 2, 4, 8

Water pollution : 3, 6, 7, 9

Soil pollution : 1, 5, 7, 10

8-2. Choose the true statements of the following :

1. Carbon monoxide decreases the concentration of oxygen in blood stream.

- Heat is not a substance but considered to be a pollutant.
- The quality of air does not vary from place to place and from time to time.
- Fertilizers are major air pollutants.
- Nitrogen dioxide is more toxic than nitrogen oxide.
- Breathing of NO_2 does not affect our health.
- Small amount of ozone in the air causes nose, eye and throat irritation.
- Addition of tetraethyl lead improves the quality of fuel.
- Polluted water causes the water borne diseases like typhoid, cholera and dysentery.
- Fruits, vegetables and grains need not be washed before they are eaten up.

Ans. True : 1, 2, 5, 7, 8, 9

8-3. Name the following :

- Something which is not a substance but is considered as a pollutant.
- Substances whose use causes water as well as soil pollution.
- The unit commonly used to represent pollutant concentration when the concentrations are small.
- The total of organic waste and waste water from homes and industries.
- Air pollution particularly associated with oxidants.
- A substance used in automobiles to control or minimize air pollutions.
- Chemical used for ripening of fruits (e.g. banana, mango).
- The compound formed from carbon monoxide and haemoglobin.
- A chemical used to improve the quality of automobiles fuel.
- Substances used to kill insects, rodents, fungi, etc in agriculture.

Ans. 1. Heat 2. Chemical fertilizers. 3. ppm. 4. Sewage 5. Smog 6. Exhaust catalyst 7. Calcium carbide 8. Carboxy haemoglobin 9. Tetraethyl lead 10. Insecticides and herbicides.

Multiple Choice Questions

84. Put (✓) mark against the appropriate choice :

- Which of the following is an air pollutant ?
(i) Sewage (ii) O_3
(iii) $(\text{NH}_4)_2\text{SO}_4$ (iv) Silver
- Which of the following if used in excess decreases the pH of the soil ?
(i) NaCl (ii) NH_4SO_4
(iii) KNO_3 (iv) Sugar
- The pollutant that combines with droplets of water in the atmosphere to produce sulphuric acid is
(i) SO_2 (ii) NH_3
(iii) CO_2 (iv) SO_3
- The unit to represent the concentration of a pollutant is
(i) g/l (ii) ppm
(iii) mole fraction
(iv) mole litre⁻¹
- Which of the following is used to improve the quality of gasoline ?
(i) Potassium chlorate
(ii) Tetraethyl lead
(iii) Manganese dioxide
(iv) Platinum
- The chemical used for ripening of fruits (e.g. banana and mango) is
(i) Calcium chloride
(ii) Ammonium nitrate
(iii) Silver nitrate
(iv) Calcium carbide

Ans. 1. (ii), 2. (ii), 3. (iv), 4. (ii), 5. (ii), 6. (iv)

8-5 Fill in the blanks.

1. is not a substance but it is considered as a pollutant.
2. Carbon monoxide is a and gas and even then it is a pollutant.
3. Excessive use of synthetic detergents is also a source for pollution.
4. Vehicles plying on roads emit lots of resulting in air pollution.
5. is the unit commonly used to represent pollutant concentration.
6. Carbon monoxide combines with haemoglobin and produces the stable compound

7. Increasing amount of CO_2 would increase the on the Earth.
8. Sulphur dioxide combines with droplets of water in the air to form
9. The emission of undesirable chemicals from automobiles can be controlled by the use of an
10. Plants clean the air by removing excess of from it.

Ans. 1. Heat 2. colourless, odourless
3. water 4. fumes 5. ppm 6. carboxy haemoglobin 7. temperature
8. sulphurous acid 9. exhaust catalyst
10. carbon dioxide.

8-6 Match the terms in column A with those in column B.**Column A**

1. Effluents
2. Biodegradable
3. B.O.D.
4. Carbon monoxide
5. Ozone
6. Platinum
7. T E L
8. Haemoglobin
9. Ammonium sulphate
10. Potassium nitrate

Column B

- (a) decreases pH of soil
- (b) improves the quality of fuel
- (c) exhaust catalyst
- (d) increases pH of soil
- (e) materials discharged into water
- (f) used by micro-organism to consume degradable material
- (g) oxygen starvation can occur
- (h) anything that can be broken down by various micro-organisms
- (i) protects the inhabitants of the Earth from high energy radiations
- (j) oxygen-carrying red pigment in blood cells

REVIEW QUESTIONS

- 8-1 What is pollution?
- 8-2 How many types of pollutions are there?
- 8-3 Define pollutant. List three major air pollutants.
- 8-4 Explain how air pollutants affect our health and property.
- 8-5 Why is carbon monoxide a potentially dangerous air pollutant?

- 8-6 Indicate the major moveable source of air pollution.
- 8-7 What is the function of an exhaust catalyst in a car?
- 8-8 With the aid of equations, indicate what happens to SO_2 once it enters the atmosphere.
- 8-9 List common air pollutants in your locality. How would you avoid air pollution at your home?

- 8-10 Define ppm.
- 8-11 Name two major sources of water pollution.
- 8-12 How do industrial wastes and sewage pollute water ?
- 8-13 What is the difference between natural pollutants and man-made pollutants of water ?
- 8-14 Suggest two ways to minimize water pollution in cities.
- 8-15 Write a short note on pollution and internal combustion engine.
- 8-16 What is a biodegradable material ?
- 8-17 Define biochemical oxygen demand (B.O.D).
- 8-18 Why is it important to know the B.O.D of a water waste ?
- 8-19. Distinguish between photochemical smog and industrial smog.
- 8-20 What is acid rain ? How does it cause soil pollution ?
- 8-21 Excessive use of fertilizers is a source of pollution. Comment on this statement.
- 8-22 Name a chemical used for ripening of fruits like banana and mango.
- 8-23 Why is it necessary to wash fruits, vegetables and grains before they are used ?
- 8-24 Why are insecticides and herbicides used in agriculture ? How do these cause soil pollution ?



